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Organic Chemistry.

Methylethyl*iso*propylmethane and Di*iso*propylmethane. G. CHAVANNE and H. DE GRAEF (*Bull. Soc. chim. Belg.*, 1924, **33**, 366—375).—Methylethyl*iso*propyl carbinol [βγ-dimethylpentan-γ-ol], prepared by the action of magnesium *iso*propyl iodide on methyl ethyl ketone, and of magnesium ethyl bromide on methyl *iso*propyl ketone, has b. p. 42—43°/11 mm., 139·4—139·9°/760 mm. (slight decomp.), d_4^{15} 0·8445, n_D^{20} 1·4280. It is converted by *p*-toluenesulphonic acid into two isomeric dimethylpentenes, probably βγ-dimethyl-Δ^{β}-pentene and βγ-dimethyl-Δ^{γ}-pentene, b. p. 92° and 96—97° respectively, which are catalytically reduced in acetic acid to *methylethyliso*propylmethane [*βγ-dimethylpentane*], b. p. 89·9—90·1°/760 mm., d_4^{15} 0·6991, d_4^{20} 0·6950, n_D^{20} 1·3918, separation point from aniline, 68·1±0·1°.

*iso*Butyl bromide is best prepared by the action of gaseous hydrogen bromide on cold *iso*butyl alcohol, the yield being 80%. Dimethyl*iso*butyl carbinol [βδ-dimethylpentan-β-ol], obtained by the action of magnesium *iso*butyl bromide on acetone, has b. p. 42—43°/11 mm., 132·8—133·4°/760 mm. (slight decomp.), d_4^{15} 0·8168, n_D^{20} 1·4172. The carbinol when dehydrated with *p*-toluenesulphonic acid gives dimethyl*iso*propylethylene [βδ-dimethyl-Δ^{β}-pentene], b. p. 83·1—83·3°/760 mm., d_4^{15} 0·6994, n_D^{20} 1·4016, the constitution of which is confirmed by oxidation with chromic acid to acetone and *iso*butyric acid. Reduction in the presence of platinum converts it into di*iso*propylmethane [βδ-dimethylpentane], b. p. 80·7—80·9°/760 mm., m. p. −119·4°, d_4^{15} 0·6769, n_D^{20} 1·3814, separation point from aniline, 78·6±0·1°. F. G. M.

Pyrogenic Dissociation of Hexadecene. H. GAULT and Y. ALTCHIDJIAN (*Compt. rend.*, 1924, **178**, 2092—2095).—The decomposition products consist of hydrogen, paraffins, and ethylenic hydrocarbons. The percentage of the last-named increases with temperature to a maximum of 67—68; further increase in temperature brings about a decrease in this yield. There is a corresponding minimum point for paraffins. The percentage of hydrogen increases slowly with rise of temperature. The authors have employed the apparatus previously described (Gault, Hessel, and Altchidjian, this vol., i, 701) and their results indicate that the size of the furnace used, whilst not altering the general results, shifts the temperature range over which they are obtained; *e.g.*, the maximum production of ethylenic hydrocarbons occurs at 570° with a 64 cm. furnace but at 685° with one of 16 cm. H. J. E.

Pyrogenic Dissociation of Hexadecane. H. GAULT and F. A. HESSEL (*Compt. rend.*, 1924, **179**, 171—173; cf. this vol., i, 701).—The pyrogenic decomposition of hexadecane at various temperatures and in furnaces of various lengths has been investig-

ated. The formation of saturated hydrocarbons and of hydrogen in the gaseous products increased and that of unsaturated hydrocarbons decreased with increase of temperature from 600° to 815°; acetylene was detected in the products at 615° and in some cases at lower temperatures. Figures are given for the iodine absorption, density, and refractive index of the liquid products; except in one instance, these contained no aromatic hydrocarbons when tested by the solubility in methyl sulphate. F. G. M.

Catalytic Activation of Ethylene by an Organo-nickelic Compound. A. Job and R. Reich (*Compt. rend.*, 1924, **179**, 330—332).—On addition of successive small quantities of pure, powdered nickel chloride to an ethereal solution of magnesium phenyl bromide in the presence of pure, dry ethylene (the temperature being maintained strictly at 6°) the gas is rapidly absorbed, the rate being proportional, not to the amount of nickel chloride added, but to the quantity of the magnesium phenyl bromide employed. By the action of water on the very complex solution obtained, the main product is ethane, mixed with smaller quantities of liquid hydrocarbons, ethylbenzene, styrene, diphenyl, and some hydrocarbons of b. p. above 270°. The action of carbon dioxide yields a mixture of acids, among which formic, propionic, and phenylpropionic acids are identified. The catalyst is probably an organonickelic compound, the magnesium acting as the acceptor.

J. W. B.

Tautomerism of Dyads. II. Acetylene and its Halogen Derivatives. (Mrs.) E. H. Ingold (*J. Chem. Soc.*, 1924, **125**, 1528—1537).—The presence of small proportions of *iso*acetylene, $CH_2{:}C$, in acetylene is indicated by the thermodynamic method for the detection of tautomeric equilibria in very mobile systems (T., 1922, **121**, 1604) and by the formation of keten when the gas is very cautiously oxidised.

Chloroacetylene exists in two phases at the ordinary temperature, since α-chloro-ββ-di-iodoethylene is produced by passing the gas into a solution of iodine in benzene, whereas exposure of the gas, mixed with nitrogen, to bright light results in the isolation of *s*-trichlorobenzene. Further, the action of hypobromous acid leads to the formation of chloroacetic acid and chlorodibromoacetaldehyde, one derived from each of the two isomerides originally in equilibrium. Bromoacetylene also displays this dual chemical character. The dihalogen-acetylenes show no tendency to pass into halogenated benzenes; all the evidence supports the *iso*acetylene structure, and no fact is known which needs an assumption of the structure $CBr{:}CBr$. A. C.

Explosion of Acetylene and Nitrogen. III. Effect of the Addition of Oxygen on the Production of Hydrocyanic Acid. W. E. Garner and S. W. Saunders (*J. Chem. Soc.*, 1924, **125**, 1634—1641; cf. T., 1921, **119**, 1903; 1922, **121**, 1729).—The relation $K_1^{II}=[HCN]/[C][N_2]^{0\cdot37}$, which gives constant values for explosive mixtures of nitrogen and acetylene alone and when

admixed with helium or hydrogen, no longer holds when oxygen is present. The production of hydrocyanic acid in explosive mixtures of acetylene, nitrogen, and oxygen, in which the content of nitrogen is kept constant at about 22% and the proportions of oxygen and acetylene are varied, increases with the proportion of oxygen, reaches a maximum in mixtures containing about 37% of oxygen, and then falls to zero. If the ratio of oxygen to acetylene exceeds 1 : 1, no hydrocyanic acid is found amongst the products; with mixtures richer in oxygen, appreciable amounts of carbon are not liberated at the temperature of the explosion and hence hydrocyanic acid cannot be formed. C. J. S.

Transformation of Acetylenic Hydrocarbons by means of Sodamide. BOURGUEL (*Compt. rend.*, 1924, **178**, 1984—1986; cf. Meunier and Desparmet, this vol., i, 701).—The action of sodamide at 110° on acetylenic hydrocarbons of the type CR:CMe results in the quantitative formation of the sodium derivatives of hydrocarbons, $CH_2R{\cdot}C{:}CH$, with the evolution of an equimolecular quantity of ammonia. The action is more rapid than when sodium alone is used (cf. Faworsky, A., 1888, 1168), and none of the hydrocarbon is reduced. A similar transformation from CR:CEt into $CH_2R{\cdot}CH_2{\cdot}C{:}CH$ occurs, but the reaction is much slower. H. J. E.

Decomposition of Ethylene Bromide by Potassium and Sodium Iodide Solutions. T. S. PATTERSON and J. ROBERTSON (*J. Chem. Soc.*, 1924, **125**, 1526—1527).—Ethylene is evolved and iodine is liberated when mixtures of potassium iodide, water, and ethylene bromide are gently boiled. S. B.

Preparation of αα-Dichloro-β-bromoethylene. H. VAN DE WALLE (*Bull. Acad. Roy. Belg.*, 1924, [v], **10**, 94—108).—This compound (cf. Denzel, A., 1879, 368) may be prepared according to the scheme: $CH_2Cl{\cdot}CH_2Cl \rightarrow CH_2{:}CHCl \rightarrow CH_2Cl{\cdot}CHCl_2 \rightarrow CH_2{:}CCl_2 \rightarrow CH_2Br{\cdot}CCl_2Br \rightarrow CHBr{:}CCl_2$. Repetition of the procedure given by Mouneyrat (A., 1899, i, 470) failed to yield *as.*-tetrachloroethane, but treatment of αβ-dichloroethane with alcoholic potassium hydroxide gives chloroethylene, which is converted by passage through cooled antimony pentachloride into ααβ-trichloroethane. Treatment of the latter with alcoholic potassium hydroxide in a current of nitrogen yields αα-dichloroethylene, which is readily brominated to αα-dichloro-αβ-dibromoethane, b. p. 175° (decomp.), 65°/13 mm., 70°/18 mm., m. p. −66·85°, d_4^{15} 2·2695, n_D^{15} 1·55930. Treatment with alcoholic potassium hydroxide solution then forms αα-dichloro-β-bromoethylene, b. p. 107—108°, m. p. −88·5°, d_4^{15} 1·9053, n_D^{15} 1·52028, which yields with alcohol an azeotropic mixture, b. p. 77·25°, containing 60·5% of alcohol. αα-Dichloro-αββ-tribromoethane, obtained by addition of bromine to the preceding compound (cf. Städel, A., 1879, 368; Denzel, *loc. cit.*), has b. p. 210° (decomp.), 106°/16 mm., m. p. 16·80°, d_4^{15} 2·6315, n_D^{20} 1·60035. αβ-Dichloro-αaβ-tribromoethane (cf. Swarts, A., 1899, i, 725) has b. p. 210° (decomp.), 112°/16 mm.,

m. p. 5·95°, d_4^{15} 2·6346, n_D^{15} 1·60846. The melting-point curve for mixtures of these two isomerides has a minimum at 4·20°, the crystalline phases being solid solutions having a gap between 80% and 100% of αβ-dichloro-ααβ-tribromoethane. T. H. P.

Action of Light on Solutions of certain Organic Substances in Chloropicrin. A. Piutti and P. Badolato (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 475—479).—Investigation of the compounds formed when solutions in chloropicrin of acetic acid, ethyl succinate, methyl salicylate, toluene, naphthalene, phenol, ψ-cumene, or *o*-, *m*-, or *p*-xylene were exposed to light for several months showed that, although chloropicrin is stable in the dark, it decomposes in the light into products having a chlorinating, oxidising, or substituting action on the solute. In some instances, the nitro group underwent reduction to the ammonium group, which separated as chloride or oxalate. T. H. P.

Halogenation of *s*.-Dipotassium Tetranitroethane. L. Hunter (*J. Chem. Soc.*, 1924, **125**, 1480—1484).—The action of chlorine on a solution of *s*.-dipotassium tetranitroethane and sodium acetate in water results in the precipitation of s.-*dichlorotetranitroethane*, $CCl(NO_2)_2{\cdot}CCl(NO_2)_2$, m. p. 107° after incipient decomposition at 60—65°. Boiling water causes it to decompose into carbon dioxide, oxides of nitrogen, hydrochloric acid, and dichlorodinitromethane. It shows the usual reactions of "positive" halogen, characteristic of the *gem*-halogen-nitroparaffins. With 50% potassium hydroxide solution it is reconverted into *s*.-dipotassium tetranitroethane. Potassium iodide solution gives the same result, iodine being precipitated. Vigorous reaction takes place with potassium cyanide: cyanogen chloride is evolved and a black powder separates, whilst the filtrate contains carbonate, nitrite, and chloride. ααβ-Tribromo-αββ-trinitroethane (cf. Scholl and Brenneisen, A., 1898, i, 345), when treated with potassium iodide, also gave *s*.-dipotassium tetranitroethane, the potassium nitrite formed by a side decomposition acting as nitrating agent. Attempts to prepare the bromine analogue of *s*.-dichlorotetranitromethane resulted in the formation of dibromodinitromethane, $CBr_2(NO_3)_2$. Although *s*.-dipotassium tetranitroethane is stable towards iodine as illustrated in the preparation of this salt from bromopicrin and potassium iodide (Hunter, T., 1923, **123**, 543), attempts to increase the yield by addition of potassium nitrite resulted in a diminished yield and production of *potassium iodonitromethane* as a by-product, orange leaflets, exploding at **154—156°**, *silver* salt, explosion point 104—106°. Salts other than potassium nitrite failed to effect this change. A. C.

Platinum Oxide as a Catalyst in the Reduction of Organic Compounds. V. Preparation of Primary Alcohols by Catalytic Hydrogenation of Aldehydes. W. H. Carothers and R. Adams.—(See i, 968.)

Action of Aluminium Sulphide on certain Organic Compounds [Ethyl Alcohol]. G. R. Levi and G. Natta.—(See i, 952.)

Dehydration of Alcohol. The System: Water–Alcohol–Hydrocarbon–Potassium Carbonate. Equilibrium between the Three Liquid Phases. L. GAY, P. MION, and SERVIGNE (*Chim. et Ind.*, May 1924 [special number], 286—295).—The equilibrium between water, liquid hydrocarbons (both pure and mixed), alcohol, and potassium carbonate is theoretically examined, the general conclusions being confirmed experimentally. The amount of alcohol in the hydrocarbon layer is independent of the potassium carbonate concentration in the lower, aqueous layer, provided this concentration is below 30%. Potassium carbonate is not sufficiently soluble at 20° to render alcohol and hydrocarbon miscible at this temperature. A good dehydrating agent must, in aqueous solution, have negligible solubility in the hydrocarbon–alcohol mixture, or the alcohol must be practically insoluble in the solution of the dehydrating agent. A sufficiently concentrated potassium carbonate solution, containing about 45% of the salt, fulfils these conditions. S. K. T.

Rotatory Dispersive Power of Organic Compounds. XII. Octyl Alcohol and Octyl Oxalate. T. M. LOWRY and E. M. RICHARDS (*J. Chem. Soc.*, 1924, **125**, 1593—1597).—Determinations of the rotatory dispersion of *sec.*-octyl alcohol for 19 wave-lengths by the visual method and 6 other wave-lengths by the photographic method have shown that the results can be expressed by one term of Drude's equation. The dispersion of octyl oxalate over a range of 27 wave-lengths is more complex and can be expressed neither by the one-term equation nor by Biot's law, although the results approximate to the latter. C. J. S.

Trimethylethylglycerol [βδ-Dimethylhexane-βγδ-triol]. PASTUREAU and H. BERNARD (*Compt. rend.*, 1924, **179**, 181—184; cf. A., 1922, i, 717; 1923, i, 646).—Magnesium ethyl bromide reacts with the chlorohydrin of mesityl oxide to give *γ-chloro-βδ-dimethylhexane-βδ-diol*, m. p. 35—37°, b. p. 105—110°/5 mm., which, on treatment with potassium carbonate, gives *βδ-dimethylhexane-βγδ-triol*, m. p. *ca.* 75°. Magnesium ethyl bromide and mesityl oxide give *βδ-dimethyl-Δ$^{\beta}$-hexan-δ-ol*, b. p. 45—47°/9 mm., which reacts vigorously with hypoiodous acid; the resulting iodohydrin is too unstable to be isolated (cf. A., 1923, i, 891). F. G. M.

Ethers of Polysaccharides with Hydroxy-acids. J. K. CHOWDHURY (*Biochem. Z.*, 1924, **148**, 76—97).—By the action of chloroacetic acid on polysaccharides in the presence of concentrated aqueous sodium hydroxide, ethers are obtained which, when thoroughly dried, are insoluble in water and in organic solvents. In the case of the cellulose ethers of glycollic acid the preparation with the lowest content of acid had one molecular proportion of the latter to three glucose residues, whilst that with the highest acid content had three molecules in each glucose residue. By the action of phosphorus tri-iodide and water on the cellulose glycollic acid ethers, cellulose and glycollic acid were obtained. In the cases of starch and inulin the highest degrees of substitution attained were respectively 2 mols. and 2½ mols. of acid per glucose residue.

The more highly substituted derivatives form insoluble salts with the alkaline-earth metals, and may be separated from the less highly substituted compounds of which the corresponding salts are soluble in water. The monosubstituted cellulose derivative exists as a lactone, that of starch as a mixture of free acid and lactone. The partly substituted cellulose derivatives may be methylated by means of methyl sulphate and sodium hydroxide, the carboxyl groups of the acid residues undergoing a partial methylation. The resulting product is soluble in cold, but insoluble in hot water. In the case of starch the carboxyl group does not undergo esterification and the product, which is soluble in both cold and hot water, shows a combined acid and methoxyl content corresponding with a substitution of $2\frac{1}{3}$ of the three available hydroxyl groups in each glucose residue. By the action of chloropropionic acid and sodium hydroxide on cellulose, lactic acid ethers were obtained in small yields, but the formation of similar products was not observed using chloro- and bromo-malonic acids. J. P.

Methylations. Hydrolysis of Methyl Sulphate. H. F. Lewis, O'N. Mason, and R. Morgan (*Ind. Eng. Chem.*, 1924, **16**, 811—812).—The reaction, $Me_2SO_4+H_2O=MeHSO_4+MeOH$, is complete within 3 mins. at 95° in mixtures of methyl sulphate and water containing from 0·5 to 75·0% of the former. The hydrolysis of the methyl hydrogen sulphate is considerably slower with concentrations of methyl sulphate up to 5%, thereafter increasing rapidly with increase in concentration of the latter, a mixture containing 75% of methyl sulphate being hydrolysed to the extent of 96% in 3 mins. In mixtures containing 1% of methyl sulphate, the presence of 1% of sulphuric or hydrochloric acid produces an initial decrease, and subsequent increase in the rate of hydrolysis as compared with water alone, these variations being less marked with 25% sulphuric acid. In mixtures containing 25% of methyl sulphate, the presence of any acid decreases the rate of hydrolysis, whilst in mixtures containing 1 or 25% of methyl sulphate, the presence of 25% of acetic acid affords almost complete resistance to hydrolysis of the methyl hydrogen sulphate. The hydrolysis is depressed by alkalis and salts, potassium hydroxide showing greater hydrolytic activity than sodium hydroxide with low concentrations of methyl sulphate, whilst potassium chloride is a stronger depressant than sodium chloride. F. G. W.

Autoxidation of Organic Sulphur Compounds. M. Delépine (*Bull. Soc. chim. Belg.*, 1924, **33**, 339—365).—A lecture delivered before the Chemical Society of Belgium. F. G. M.

Method of Preparing Sulphinones. L. Bert (*Compt. rend.*, 1924, **178**, 1826—1828).—*Di*-n-*butyl sulphite*, a colourless liquid, b. p. 230° (slight decomp.), 111°/15 mm., d^{14} 1·001, n_D^{14} 1·435, was prepared by the action of sulphur chloride on butyl alcohol at 100°. When 1 mol. is added to 2 mols. of an organo-magnesium compound of the type MgRX, the corresponding sulphinone R_2SO is obtained. H. J. E.

Action of Diazo Salts on Methanesulphonamide. P. K. Dutt (*J. Chem. Soc.*, 1924, **125**, 1463—1465; cf. T., 1921, **119**, 2088).—Methanesulphonamide, m. p. 84—85°, was prepared by slowly dropping methyl sulphate into a mixture of a solution of sodium sulphite and boiling methyl alcohol and treating the sodium methanesulphonate (yield *ca.* 94%) successively with phosphoryl chloride and dry ammonia. When it is dissolved in sodium hydroxide and mixed with a solution of benzenediazonium chloride, a yellow solid appears which quickly decomposes and produces phenylazoimide. After the removal of the latter, the aqueous portion is treated with a second portion of benzenediazonium chloride equal to that first used, whereby the *compound*,

$$Me{\cdot}SO_2{\cdot}N{:}NPh,$$

yellow needles, m. p. 71—72° (decomp.), is produced. The *substance*, $Me{\cdot}SO_2{\cdot}N{:}N{\cdot}C_7H_7$, prepared similarly from *p*-toluenediazonium chloride, has m. p. 112—113° (decomp.). The interaction of toluene-ω-sulphonamide with benzenediazonium chloride gave a tarry product from which only phenylazoimide could be isolated. The stability of these diazoamines appears to depend on some influence at present unknown. A. C.

Thermal Decomposition of some Pure Metallic Acetates. W. Krönig (*Z. angew. Chem.*, 1924, **37**, 667—672).—The dried acetates of lithium, sodium, potassium, copper, magnesium, calcium, barium, lead, and manganese, when gradually heated to 500°, appear normally to break down directly into acetone, metal oxide, and carbon dioxide, the last two then combining to a greater or less extent. The best yield of acetone is given by lithium acetate, the residue being almost pure lithium carbonate. Sodium, potassium, calcium, and barium acetates also give a residue consisting essentially of metallic carbonate, but the distillate from the first two contains a large amount (37% and 52%, respectively) of an oily condensation product, insoluble in water. The decomposition of copper acetate resembles that of silver acetate, the residue comprising the metal (with a small quantity of oxide) and carbon, and the distillate nearly pure acetic acid. Magnesium and manganese acetates yield mainly the metallic oxide, acetone, and carbon dioxide. With lead acetate, the lead oxide first formed oxidises a portion of the acetone, and the residue consists of nearly pure lead. An examination of the thermal decomposition of zinc acetate was impossible owing to excessive sublimation. The yield of acetone from metallic acetates appears to be related to the basicity of the metal. W. T. K. B.

Hydrates in Aqueous Solution. II. Citrate, *d*-Tartrate, Acetate, and Oxalate Ions. R. Fricke and H. Schützdeller (*Z. anorg. Chem.*, 1924, **136**, 295—304).—Determinations of the viscosity, freezing point, and density of aqueous solutions of the neutral potassium salts of citric, *d*-tartaric, acetic, and oxalic acids of varying concentrations indicate that the anions, especially the first three, are strongly hydrated. Hofmeister's series of

decreasing hydration—citrate, tartrate, sulphate, acetate—is true only if solutions of equimolar concentration are compared; it does not hold for solutions of equal normality. The molar depression of the freezing point of solutions of potassium oxalate or tartrate falls continuously with increasing dilution, whereas that of solutions of potassium citrate or acetate has a minimum value. Normal potassium citrate ($+H_2O$) has d_4^{18} 1·995 and fused potassium acetate d_4^{18} 1·519. A. R. P.

Marine Animal Oils. Identity of Phocenic and Valeric Acids. E. André (*Bull. Soc. chim.*, 1924, [iv], **35**, 857—868).—Phocenic acid, derived from dolphin's head or whale oil by hydrolysis, is shown to be identical with valeric acid. The author thus refutes the suggestions made both by Lewkowitsch ("Chemical Technology of Oils, Fats and Waxes," 5th ed., p. 152) and Fryer and Weston ("Technical Handbook of Oils, Fats and Waxes," 3rd ed., p. 37) that the oil consists of a mixture of the glycerides of *n*-butyric and hexoic acids. A. E. C.

Oil from *Mimusops Hexandra*: Rayan Oil. C. K. Patel (*J. Indian Inst. Sci.*, 1924, **7**, 71—80).—Rayan seeds yield 24·6% of an edible oil which is equivalent to a yield of 47·2% on the kernels. The oil, $d_{15·5}^{15·5}$ 0·914, n_D^{60} 1·4528, saponification value 190, iodine value 65, has a faint odour, is nearly colourless, is readily refined by alkali, and is easily hydrolysed by castor-seed lipase. The curve relating iodine value with refractive index is exactly similar to those for mohua, cotton-seed, and cashew-kernel oils. The fatty acids obtained by hydrolysis are palmitic, stearic, and oleic, with very small amounts of lignoceric and linolic, and the unsaponifiable matter consists of a liquid with a high refractive index and a sterol, probably ergosterol. The oil also contains a small quantity of a bitter principle soluble in water, probably a saponin. P. M.

Dehydrogenating Action of Nickel–Copper Catalysts. G. Kita, T. Mazume, and K. Kino (*Chem. Umschau*, 1924, **31**, 165—167).—Catalysts were used containing 16·9% of Ni and 3·1% of Cu; 14·0% of Ni and 6·0% of Cu; and 10·5% of Ni and 9·5% of Cu on kaolin. Stearic acid at 300—310° does not undergo dehydrogenation, but ketonic decomposition takes place, the amount increasing with increase of copper in the catalyst. With herring oil, dehydrogenation of the fatty acid takes place at 200° and at 170° with those catalysts containing more copper, and hydrogenation with those containing only nickel or nickel and a little copper. The catalyst containing little copper shows slight dehydrogenation at 100°. The temperature of reduction of the catalyst has an important effect; that reduced at 340—350° shows some dehydrogenating activity even at 100°, but that reduced at 220—230° shows none at any of the temperatures employed. P. M.

Wool Fat. F. Grassow (*Biochem. Z.*, 1924, **148**, 61—75).—By hydrolysis of wool fat with *N*/2-potassium hydroxide, cerotic acid,

$C_{27}H_{54}O_2$, m. p. 78°, was obtained and identified by comparison, together with its derivatives (methyl, ethyl, and cholesteryl esters, amide, *anilide*, m. p. 97°) with a corresponding preparation from beeswax. The *menthyl* ester, m. p. 43—44°, and the *phenyl* ester, plates, m. p. 59°, are described. *Methyl* and *benzyl lanocerinates*, m. p. 79—80° and 80°, respectively, are also described. By the action of benzoyl chloride on the silver lanocerinate, the mixed *anhydride*, $C_{29}H_{57}(OH)_2{\cdot}CO{\cdot}OBz$, m. p. 76°, was obtained.

J. P.

Decomposition of Animal Wax. A. MAILHE (*Compt. rend.*, 1924, **179**, 184—185).—A mixture of 300 g. of beeswax, m. p. 64°, and 50 g. of anhydrous magnesium chloride was cautiously heated. At the beginning of the reaction the gas evolved contained CO_2 39%, CO 25·5%, CH_4 9%, and H_2 26·5%. As the temperature rose to 500°, about 215 g. of distillate were collected, whilst a sample of the gas evolved contained CO_2 14·5%, CO 22·4%, olefines 23·5%, methane 17·4%, other paraffins 18%, and H_2 4·2%. The distillate, when freed from acids, had b. p. 55—350°, and contained paraffins, olefines, and an unidentified ketone, white needles, m. p. 53—54°. Zinc, calcium, and barium chlorides and metallic oxides gave similar results.

F. G. M.

Action of Halogens on Unsaturated Aliphatic Compounds. J. J. CERDEIRAS (*Bull. Soc. chim.*, 1924, [iv], **35**, 902—904).—Wijs' reagent is 3—4 times more reactive than iodine in acetic acid solution towards olive and linseed oils, and 2—3 times as reactive towards oleic and linolenic acids. In each case, the reaction with Wijs' reagent is practically complete after 40 mins.

A. E. C.

Natural Soaps in Soja Bean. S. MURAMATSU (*J. Chem. Soc. Japan*, 1923, **44**, 1035—1049).—When powdered soja bean, after being freed from fats and free acids, is extracted with warm alcohol (80%), the amount of soaps dissolved in the case of different species of the bean (even when unripe) is 1·44—1·86% of the dried bean. The total acids of the soap are composed of fatty and hydroxy-acids. The mixed fatty acids have acid value 177·1; mean mol. wt. 316·9. They can be separated into liquid acids, m. p. 38° (29·31% of the total organic acid), and solid acids, m. p. 55° (4·63%). The purified hydroxy-acid, $C_{34}H_{68}O_{17}$, white crystals, m. p. 224°, is named *hispidic acid*. It gives a *hexa-acetyl* derivative, m. p. 155°. The alkali salts of hispidic acid easily give a viscous, aqueous solution, which has marked foam-forming and detergent powers.

K. K.

Relation between the Iodine Values and Refractive Indices of Hardened Oils. II. H. E. WATSON and J. J. SUDBOROUGH (*J. Indian Inst. Sci.*, 1924, **7**, 81—95).—Iodine values and refractive indices for oils of different degrees of hydrogenation are recorded for argemone, English mustard, Indian rape, cashew kernel, soja bean, poppy-seed, rayan, olive, seal, and cod-liver oils. Rocket, mustard, and rape oils have higher refractive indices for a given

iodine value than all the other oils examined except castor and argemone oils, this being attributed to the presence of glycerides of erucic acid. The high ratio of refractive index to iodine value for argemone oil is not due to glycerides of erucic acid, but to diglycerides and glycerides of hydroxy-acids. The refractive index for completely hardened olive oil (n_D^{60} 1·4463) agrees very closely with that of the purest tristearin (1·4462). Most of the curves are approximately parallel, but that for seal oil is exceptional and crosses most of the others. P. M.

Theory of Polymerisation in Fatty Oils. II. R. S. Morrell (*J. Oil and Colour Chem. Assoc.*, 1924, **7**, 153—160).—The degree of polymerisation of fatty oils is not accurately indicated by the determination of the iodine value on account of the depolymerising action of some of the components of Wijs' solution. The molecular weight of these oils cannot be satisfactorily determined with benzene as a solvent, as esters show a tendency to combine with the solvent, and association occurs if acids be present. The polymerisation of linseed oil may be extramolecular as well as intramolecular, and it must be viewed from a colloidal as well as from a strictly chemical aspect. The ethyl esters derived from linseed and tung oils show a greater gain in weight in "drying" than do the glycerides, but the resulting films are liquid, and not solid as in the latter case, where polymerisation followed by gelation takes place. There is absorption of oxygen in both cases. P. M.

Equilibrium between Lactic Acid and its Anhydrides. G. I. Thurmond and G. Edgar (*Ind. Eng. Chem.*, 1924, **16**, 823—826).—In a mixture of lactic acid, lactic anhydride, and lactide, the free acid is determined by direct titration of an alcoholic solution of the mixture with 0·3*N*-sodium hydroxide, and the total of the three constituents by the consumption of alkali when the mixture is heated for 15 mins. with excess of the reagent. When warmed in alcoholic solution with zinc carbonate, the free acid and anhydride are precipitated as zinc lactate, the unattacked lactide being then determined in the evaporated and filtered solution by warming with excess of standard alkali, adding a known excess of standard acid and a little potassium ferrocyanide to precipitate the last traces of zinc, and titrating back. The presence of zinc interferes with the end-point of this titration, and the amount of zinc held in solution varies with the amount of lactide present. Lactic acid, lactide, and water form an equilibrium mixture, the position of the equilibrium being the same at 155°, for which $C_{\text{lactide}} \times C^2_{H_2O}/C^2_{\text{acid}} = 0{\cdot}0567$. Anhydride is present in such mixtures in amount varying with the previous history of the sample, and not depending on the amount of water present, an effect ascribed to the colloidal nature of the anhydride. F. G. W.

Spontaneous Oxidation of Lactic Esters and Alanine in Presence and in Absence of Catalysts. L. J. Simon and L. Piaux (*Bull. Soc. Chim. biol.*, 1924, **6**, 412—423).—Lactic esters

are oxidised spontaneously in contact with air or oxygen with the formation of acetaldehyde, ethyl pyruvate, and carbon dioxide. The oxidation is accelerated by warming and agitation, but it is not influenced by light. Alanine, on the other hand, is not spontaneously oxidised except in the presence of sodium hydroxide and finely-divided metallic copper, when it gives rise to pyruvic acid and acetaldehyde. If pyruvates in alkaline solution are agitated in presence of oxygen, a decrease in the quantity of pyruvic acid is observed. The production of pyruvic acid does not necessarily precede the formation of acetaldehyde, which may be derived from α-hydroxyacrylic acid. D. R. N.

Synthesis of Oxalic Acid. C. MATIGNON and C. FAURHOLT (*Compt. rend.*, 1924, **179**, 271—274).—The synthesis of potassium oxalate by the action of carbon monoxide under pressure on potassium carbonate is described. The reverse action, viz., the decomposition of the oxalate in a vacuum, is observed at 370°, is distinct at 420°, and reaches a practicable velocity at 430—440°; for the synthesis it is therefore necessary to employ at least this temperature and a pressure of carbon monoxide greater than that calculated either by the Q/T relation or the Nernst formula from the equation $CO+K_2CO_3=K_2C_2O_4+19{\cdot}8$ cals. At the necessary temperature in the absence of catalysts, the decomposition of the carbon monoxide into carbon dioxide is negligibly small, so that at 470° and with a pressure of 243 atm. of carbon monoxide, potassium carbonate to which is added 2·5% of animal charcoal as a catalyst, is converted in 2½ hours into a product containing 29% (optimum) of potassium oxalate. Under the same conditions, but in the absence of animal charcoal, the yield is only 9·7%. No oxalate is produced under similar conditions using sodium carbonate, since the thermal effect necessitates the use of a much higher pressure. J. W. B.

Complex Compounds of Chromium and Cobalt with Aliphatic and Aromatic Amines. IV. Stereochemistry of Saturated Tervalent Nitrogen. J. MEISENHEIMER (*Annalen*, 1924, **438**, 217—278).—[With L. ANGERMANN and H. HOLSTEN.]—*Pyridochromidioxalates.* trans-*Pyridinium diaquochromidioxalate*, $[Cr(C_2O_4)_2(H_2O)_2]H,C_5H_5N$, (I), fine, lilac crystals, is obtained by double decomposition of the sodium salt with pyridinium nitrate, the *cis* salt being present in the mother-liquors. The *cis* salts of this series are transformed into the *trans* salts in dilute hydrochloric acid solution, the reverse change being brought about by dilute alkalis. Compound (I) is converted into trans-*pyridinium monoaquomonopyridochromidioxalate*, $[Cr(C_2O_4)_2(H_2O)Py]H,C_5H_5N$, reddish-violet crystals, by the action of cold aqueous pyridine, the *cis isomeride* being obtained if excess of pyridine, with only a trace of water, is used. The *dipyridochromidioxalates*, $[Cr(C_2O_4)_2(C_5H_5N)_2]$, are obtained from the diaquo salts when the latter are boiled with pyridine, *cis-trans* isomerism not being observed in this series, the following members of which are described: *potassium*, pale rose needles ($+3H_2O$) or octahedra ($+2H_2O$); *pyridinium* ($+2\frac{1}{2}H_2O$);

sodium ($+1H_2O$); *barium* and *calcium* ($+6H_2O$); *cinchonine*, and *strychnine* salts. *Sodium tripyridochromidioxalate*,

$$[Cr(C_2O_4)_2(C_5H_5N)_3]Na,$$

bluish-red, cubic crystals (anhydrous) or prisms ($+3\frac{1}{2}H_2O$), is obtained by boiling the dried diaquo salts with anhydrous pyridine. The complex *aniline* and *cinchonine* salts are described.

Dimethylethylenediaminechromidioxalates. *Ethylene di-p-toluenesulphonamide*, prisms, m. p. 162—163°, was treated with methyl sulphate and sodium hydroxide to form *ethylene di-p-toluenesulphonmethylamide*, needles, m. p. 167—168°, the latter yielding dimethylethylenediamine on hydrolysis with 70% sulphuric acid. *Potassium dimethylethylenediaminechromidioxalate* was isolated in the form of a double salt with potassium iodide, $[Cr(C_2O_4)_2C_4H_{12}N_2]K,KI,2H_2O$, small, dark red crystals, by the action of the base on an aqueous solution of *cis* potassium diaquochromidioxalate at 70°, potassium iodide being added when reaction was complete. The *potassium nitrate double* salt, $[Cr(C_2O_4)_2C_4H_{12}N_2]K,KNO_3,2H_2O$, dark red plates or prisms, the *silver* salt, $[Cr(C_2O_4)_2C_4H_{12}N_2]Ag,H_2O$, bluish-red plates, and the *strychnine* salt, bluish-red needles, are described.

[With E. KIDERLEN.]—*Chloroaminediethylenediamine cobalti* salts. *Praseo*-dichloroethylenediaminecobalti salts react in cold aqueous solution with primary aliphatic and aromatic amines, one of the inner halogen atoms being replaced by the amine. The *violeo* salts yield identical products, but the reaction is much slower. *Chloroanilinediethylenediamine cobaltichloride*, $[Co\ en_2,Ph{\cdot}NH_2,Cl]Cl_2,H_2O$, reddish-violet, hexagonal prisms; *bromide* ($+\frac{1}{2}H_2O$), similar; *iodide*, *chloride-dithionate*, violet-pink prisms; *nitrate*, dark red crystals; *chloride-nitrate*, violet-pink needles; and d-*π-bromocamphorsulphonate* are described. The *p*-toluidine derivatives of this series decompose more readily than those of aniline. *Chloro-p-toluidine diethylenediaminecobaltichloride* ($+H_2O$), *bromide* ($+H_2O$), *iodide*, *dithionate*, *chloride-nitrate*, and d-*π-bromocamphorsulphonate* are described. The tendency of primary amines to enter the complex ion increases with increasing basicity, aliphatic amines reacting more rapidly than aromatic. *Chloroallylamine diethylenediamine cobaltichloride*, $[Co\ en_2(C_3H_7N)Cl]Cl_2,H_2O$, *bromide*, *iodide*, *dithionate*, and d-*π-bromocamphorsulphonate* ($+2H_2O$), are described. The latter could not be resolved by fractional crystallisation. *Chlorobenzylaminediethylenediamine cobaltichloride*,

$$[Co\ en_2(C_7H_9N)Cl]Cl_2{\cdot}H_2O,$$

violet-red needles (anhydrous, lustrous pink plates), *bromide* ($+\frac{1}{2}H_2O$), *iodide*, *chloride-dithionate*, *nitrate*, and d-*π-bromocamphorsulphonate*, m. p. 183—185° (decomp.), are described. The latter was separated into the inactive (*trans*) form and *d*- and *l*-(*cis*) forms. *Chloro-ethylaminediethylenediamine cobaltichloride*,

$$[Co\ en_2(C_2H_7N)Cl]Cl_2,H_2O,$$

and *iodide* (anhydrous) were also prepared. The action of benzylamine and ethylamine on the *violeo* salts yields hydroxo-aquo salts. Diethylamine and methylbenzylamine react with *praseo*-chloride with formation of trans*chlorohydroxodiethylenediamine cobaltichloride*, $[Co\ en_2(OH)Cl]Cl,H_2O$, dove-grey crystals (an-

hydrous, paler and greenish). This yields, on solution in hydrochloric acid, trans*chloroaquodiethylenediamine cobaltichloride*, $[Co\ en_2(H_2O)Cl]Cl_2,H_2O$, dirty, greyish-green needles; on warming with aqueous potassium bromide, *hydroxoaquodiethylenediamine cobaltibromide*, $[Co\ en_2(OH)(H_2O)]Br_2$; and on precipitation from warm aqueous solution with alcohol, *diaquodiethylenediamine cobaltichloride*, $[Co\ en_2(H_2O)_2]Cl_3,2H_2O$, short, red, hexagonal prisms. Dimethylethylenediamine converts the *praseo*-chloride into triethylenediamine cobaltichloride, whilst methylaniline converts it into the *violeo*-chloride and the *complex salt*,

$$[Co_2\ en_5Cl_2]Cl_4,H_2O.$$

[With L. ANGERMANN and H. HOLSTEN.]—*Glycine and sarcosine diethylenediamine cobalti salts. Glycinediethylenediamine cobaltichloride*, $[Co\ en_2(C_2H_4O_2N)]Cl_2,H_2O$, yellowish-red prisms, is obtained by the action of glycine on *praseo*-chloride in presence of sodium carbonate. The d-π-*bromocamphorsulphonate*, thick red prisms, yields the l-*complex* d-*bromocamphorsulphonate* on repeated crystallisation from alcohol and water. The l-*iodide* and l-*dithionate* are described. *Sarcosinediethylenediamine cobaltichloride*,

$$[Co\ en_2(C_3H_6O_2N)]Cl_2,1\tfrac{1}{2}H_2O,$$

strawberry-red plates, is obtained similarly, using sodium hydroxide in place of the carbonate. The *iodide* ($+1H_2O$) and *dithionate* ($+1H_2O$) were also prepared. The d-*bromocamphorsulphonate* forms pale red needles or garnet-red prisms containing alcohol and water of crystallisation, or pink needles of the heptahydrate. The latter can be obtained in two forms of $[M]_D$ $-923°$ and $+2020°$, respectively, the optical activity of the complex ion being due to the cobalt atom alone, the asymmetric nitrogen atom of the sarcosine being inactive. When the mother-liquors from the above salts were concentrated, a *tetrahydrate* separated as a pale red powder, the freshly prepared solution of which had $[M]_D$ $+2290°$, the value rapidly falling to $+2020°$, the increased activity being due to the nitrogen atom. The remaining isomerides were only obtained in an impure condition. The d- and l-*iodides* ($+1\frac{1}{2}H_2O$), red prisms, $[M]_D$ $+1485°$ and $-1530°$, and *dithionates* ($+1H_2O$), $[M]_D$ $+1530°$ and $-1555°$, are described. The action of phenylglycine, *o*-carboxyphenylglycine, and anthranilic acid on the *praseo*-chloride did not proceed analogously to that of the above bases. F. G. W.

Ethyl-*n*-hexylbarbituric Acid and other Derivatives of *n*-Hexylmalonic Acid. A. W. DOX (*J. Amer. Chem. Soc.*, 1924, 46, 1707—1711).—*n*-Hexyl bromide condenses with ethyl malonate in the presence of sodium ethoxide, giving *ethyl* n-*hexylmalonate*, b. p. 268—270°/749 mm., from which n-*hexylmalonic acid*, m. p. 105—106° (*amide*, m. p. 208°, *anilide*, m. p. 156°), is obtained by hydrolysis with potassium hydroxide. On heating with carbamide and sodium ethoxide at 104°, ethyl hexylmalonate yields n-*hexylbarbituric acid*, m. p. 216°. Methylcarbamide similarly yields 1-*methyl*-5-n-*hexylbarbituric acid*, m. p. 68°. 1-*Phenyl*-5-n-*hexylbarbituric acid*, m. p. 141°, and 1-o-*tolyl*-n-*hexylbarbituric acid*, m. p. 118°, were similarly prepared. *Ethyl ethyl*-n-*hexylmalonate*,

b. p. 280—282°/755 mm., from ethyl ethylmalonate and hexyl bromide, yields *ethyl*-n-*hexylmalonic acid*, m. p. 75°, decomp. at 140°. The ester is converted by carbamide and sodium ethoxide into *ethyl*-n-*hexylbarbituric acid*, small, white crystals, in 96% of the theoretical yield. Ethyl-*n*-hexylbarbituric acid is a somewhat more effective hypnotic than "luminal," being more rapid in its action and less toxic, although the effect is of shorter duration. 1-Methyl-5-hexylbarbituric acid is inert and 1-phenyl-5-hexylbarbituric acid is toxic without hypnotic action. R. B.

Carbon Suboxide. O. DIELS, R. BECKMANN, and G. TÖNNIES (*Annalen*, 1924, **439**, 76—96).—Carbon suboxide was prepared by a modification of the method of Ott and Schmidt (cf. A., 1922, ii, 641) which increased the yield from 40 to 55—60%. The hypothesis of Ott and Schmidt that the lack of stability of carbon suboxide, prepared by means of phosphoric oxide, is due to the presence of phosphorus compounds is shown to be incorrect, since specimens prepared from diacetyltartaric anhydride were found to polymerise as rapidly as those obtained by the older method, the stability of Ott and Schmidt's specimens more probably being due to the careful removal of other substances, *e.g.*, acetic acid. By the action of carbon suboxide on acetic acid, a product is obtained which, by loss of acetic anhydride, yields not malonic anhydride as previously suggested (cf. A., 1908, i, 929), but a *mixed anhydride* of acetic and malonic acids, $CO_2H{\cdot}CH_2{\cdot}CO{\cdot}OAc$. With oxalic acid in acetone solution, carbon suboxide yields the β-lactone of β-hydroxy*iso*propylmalonic acid (cf. Meldrum, T., 1908, **93**, 601), carbon dioxide and carbon monoxide also being evolved. Malonic acid in ether or ethyl acetate solutions reacts with 3 mols. of carbon suboxide, probably first to yield a mixed anhydride of keten character, which then reacts with the remaining 2 mols. of the suboxide to yield an exceedingly hygroscopic, yellow *substance* (decomp. 60°) to which the formula

$$CO_2H{\cdot}CH_2{\cdot}CO{\cdot}O{\cdot}OC{>}\overset{H}{C}{<}\overset{CO}{CO}{>}C{<}\overset{CO}{CO}{>}C{<}\overset{CO}{CO}{>}C{<}\overset{H}{CO{\cdot}O{\cdot}CO{\cdot}CH_2{\cdot}CO_2H}$$

is given. It reacts with water, yielding carbon dioxide and malonic acid and with alcohols it yields esters of the acid

$$CO_2H{>}\overset{H}{C}{<}\overset{CO}{CO}{>}C{<}\overset{CO}{CO}{>}C{<}\overset{CO}{CO}{>}C{<}\overset{H}{CO_2H},$$

together with the corresponding dialkyl esters of malonic acid and acetonedicarboxylic acid (the latter by profound alcoholysis); the *methyl*, m. p. 183·5° (decomp.); *ethyl*, m. p. 150—151° (decomp.); *propyl*, m. p. 132—133°, esters are described. Molecular-weight determinations agree with the suggested formula, and hence the constitution of the corresponding red polymeride of carbon suboxide is probably best represented by the formula,

$$O{:}C{:}C{<}\overset{CO}{CO}{>}\left[C{<}\overset{CO}{CO}{>}C\right]_x{<}\overset{CO}{CO}{>}C{:}C{:}O.$$

The reaction of carbon suboxide with hydrogen sulphide depends largely on the proportions of the reactants employed. With excess of hydrogen sulphide, thioacetic acid and carbonyl sulphide are formed, dithiomalonic acid probably being an intermediate product.

In equimolecular proportion, the reaction yields *bi(?)molecular malonic thioanhydride*, $H_2C<^{CO\cdot S\cdot CO}_{CO\cdot S\cdot CO}>CH_2$, m. p. 120—125°, its very slight solubility in all solvents precluding the determination of its molecular weight. With ammonia, it yields the *ammonium* salt of *thiomalonamic acid*, but with aniline yields only malonanilide, hydrogen sulphide being evolved. Heating in a high vacuum at 200° yields carbonyl sulphide and thioacetic acid. Thermal decomposition in the presence of phosphoric oxide yields carbon suboxide, hydrogen sulphide, carbonyl sulphide, carbon subsulphide, and the *unimolecular malonic thioanhydride*, $CH_2<^{CO}_{CO}>S$, dark golden, very unstable crystals, m. p. 60°. It has a distinct acid character and reacts with dimethylaniline in dry benzene with evolution of heat, and is therefore probably *ketenthiocarbonic acid*, CO:CH·CO·SH. With water, much heat is evolved and malonic acid is formed with evolution of hydrogen sulphide, but if the mixture be kept cool in ice no hydrogen sulphide is formed and *monothiomalonic acid*, a crystalline compound, is produced. This on heating with water yields malonic acid and hydrogen sulphide.

J. W. B.

Configuration of αα′-Dibromodibasic Acids. II. Derivatives of Adipic Acid. A. W. Bernton, H. R. Ing, and W. H. Perkin, jun. (*J. Chem. Soc.*, 1924, **125**, 1492—1502).—Isomeric ethyl and methyl αα′-dibromoadipates have been prepared and condensed with ethyl sodiomalonate and similar compounds to form *cyclo*pentanes. Further evidence is adduced in support of the contention (cf. T., 1921, **119**, 1393) that the αα′-dibromoadipic acid of m. p. 193° is the *dl*- or racemic modification and that of m. p. 139° the *meso*-isomeride. The liquid isomeride of ethyl αα′-dibromoadipate on condensation with ethyl sodiomalonate yielded ethyl *cyclo*pentane-1 : 2 : 2 : 3-tetracarboxylate, which on hydrolysis gave a solid, m. p. 184°, identical with the *cyclo*pentane-1 : 2 : 3-tricarboxylic acid obtained by Perkin and Robinson (*loc. cit.*) from the solid isomeride. The tribasic acid when treated successively with thionyl chloride and concentrated ammonia gave the *triamide*, m. p. 274°. The solid and liquid isomerides of methyl dibromoadipate on condensation with ethyl sodiomalonate formed (in each case) *methyl* cyclo*pentane*-1 : 2 : 2 : 3-*tetracarboxylate*, m. p. 82—84°. Hydrolysis with methyl-alcoholic potassium hydroxide gave *trans*- (m. p. 184°), and with boiling hydrochloric acid a mixture (m. p. *ca.* 154°) of *cis*- and *trans-cyclo*pentanetricarboxylic acids. *Ethyl* 2-*acetyl*cyclo*pentane*-1 : 2 : 3-*tricarboxylate*, b. p. 181—190°/16 mm., was obtained on condensing the solid isomeride of ethyl dibromoadipate with ethyl sodioacetoacetate; on hydrolysis, it yielded *trans-cyclo*pentane-1 : 2 : 3-tricarboxylic acid. Ethyl sodiobenzoylacetate and the solid isomeride yielded *ethyl* 2-*benzoyl* cyclo*pentane*-1 : 2 : 3-*tricarboxylate*, an oil, b. p. 235—242°/14 mm.; hydrolysis with cold methyl-alcoholic potassium hydroxide gave the trans-cyclo*pentane*-1 : 2 : 3-*tricarboxylate* (the benzoyl group hav-

ing been eliminated); the liquid isomeride gave the same products. Both isomerides of methyl αα′-dibromoadipate react with methyl sodiocyanoacetate to form *methyl* 2-*cyano*cyclo*pentane*-1 : 2 : 3-*tricarboxylate*, rhombic prisms, m. p. 83—84°, b. p. 192—196°/12 mm. Cold concentrated hydrochloric acid converts this into the *dimethyl* cyclo*pentanetetracarboxylate*, m. p. 115°. With boiling acid, a mixture of the *cis* and *trans* forms of the *cyclo*pentane-1 : 2 : 3-tricarboxylic acid was obtained. The *liquid isomeride* of *methyl αα′-dibromoadipate* (cf. Stephen and Weizmann, T., 1913, **103**, 271), b. p. 169—170°/14 mm., is converted to the extent of about 50% into the higher melting isomeride during distillation; the change takes place very gradually at the ordinary temperature. The liquid isomeride of ethyl dibromoadipate behaves similarly, but the conversion is more rapid. Sodium ethoxide or methoxide readily brings about the transformation. Two isomeric *methyl αα′-di-iodoadipates*, m. p. 63° and 112°, respectively, were prepared by boiling the dibromo compounds with sodium iodide in methyl-alcoholic solution. The former was almost immediately changed to the latter variety when its solution in methyl alcohol was shaken with 2 mols. of sodium methoxide. Potassium hydroxide in alcohol acts equally well, but the change was much more gradual in the presence of alcoholic ammonia. The di-iodo ethyl esters interacted much less readily with ethyl sodiomalonate than the corresponding dibromo esters. Prolonged boiling of the low-melting isomeride of methyl di-iodoadipate with methyl sodiocyanoacetate gave a small yield of methyl 2-cyano*cyclo*pentane-1 : 2 : 3-tricarboxylate, and the methyl di-iodoadipate which was recovered had been transformed into a variety of high m. p. The *diamide* of *αα′-di-iodoadipic acid*, m. p. 238° (decomp.), was obtained by the action of concentrated methyl-alcoholic ammonia on methyl di-iodoadipate. Both isomerides of methyl dibromoadipate gave the *diamide* of *αα′-dibromoadipic acid*, m. p. 196°. A. C.

Compounds of Malic Acid and Copper. E. Darmois (*Compt. rend.*, 1924, **178**, 1981—1983).—Addition of copper hydroxide to solutions of malic acid resulted in formation of two well-defined salts, $Cu(C_4H_4O_5)_2,2H_2O$, sky-blue crystals, and

$$3CuO,2C_4H_6O_5,4H_2O,$$

green crystals. In the attempt to obtain other salts, some physical properties of the solutions obtained by adding various proportions of copper hydroxide to malic acid were studied, and details of the values obtained are given. H. J. E.

Rotatory Dispersive Power of Organic Compounds. XI. Molecular Weight of Ethyl Tartrate and the Origin of Anomalous Rotatory Dispersion in Tartaric Acid and its Derivatives. T. M. Lowry and J. O. Cutter (*J. Chem. Soc.*, 1924, **125**, 1465—1470).—Measurements of molecular weight and optical rotation of ethyl tartrate in various solvents did not show any parallelism between the rotation and the degree of association of the solute. The authors therefore criticise the suggestion of

Astbury (A., 1923, i, 178) that the dextrorotatory component of tartaric acid is a single molecule, whilst the lævorotatory component is a polymeride in which the structure of the crystal is in part maintained. Anomalous rotatory dispersion is ascribed to intramolecular changes. S. B.

Optical Superposition. V. *d-sec.*-Octyl *i*-Tartrate. T. S. PATTERSON and C. BUCHANAN (*J. Chem. Soc.*, 1924, **125**, 1475—1476).—d-sec.-*Octyl* i-*tartrate* has b. p. 208°/about 4 mm., m. p. 33°, $[\alpha]_D^{17}$ +0·42°. This value of the specific rotation is in contradiction to the principle of optical superposition. S. B.

Dithioformic Acid. T. G. LEVI (*Gazzetta*, 1924, **54**, 395—397).—From potassium dithioformate solution, prepared by the action of potassium sulphide on chloroform (cf. Cambi, *R. Ist. Lomb. Sci. Lett.*, 1910, **43**, II), the corresponding *silver*, $H{\cdot}CS_2Ag$, and *lead* salts may be obtained as comparatively stable, orange-yellow precipitates; the former begins to darken at 95—100° and the latter at 130—135°. The *zinc* salt is yellowish-white and the *cobalt* salt, deep reddish-brown. The *disulphide*, $(H{\cdot}CS_2{\cdot}CS_2{\cdot}H)_x$, obtained on cautious addition of alcoholic iodine solution to potassium dithioformate dissolved in alcohol, forms a reddish-yellow precipitate, decomp. above 200°. T. H. P.

Preparation of Thioacetic Acid. H. T. CLARKE and W. W. HARTMAN (*J. Amer. Chem. Soc.*, 1924, **46**, 1731—1733).—Acetic anhydride or acetyl chloride alone does not react with hydrogen sulphide, but on passing the gas into acetic anhydride containing about 2% of acetyl chloride absorption takes place to the extent of 80% of the quantity calculated on the equation: $(CH_3CO)_2O+H_2S=Me{\cdot}CO{\cdot}SH+Me{\cdot}CO_2H$, and a 70% yield of thioacetic acid, b. p. 88—91·5°, is obtained. Hydrogen chloride and concentrated sulphuric acid also catalyse the reaction, the latter acid also tending to oxidise the hydrogen sulphide, but acetyl bromide is a more effective catalyst than acetyl chloride (cf. Orton, Watson, and Bayliss, T., 1923, **123**, 3081). The reaction proceeds in two stages, the first of which (20—30% absorption) requires only one-tenth of the amount of catalyst required for completion of the reaction. R. B.

Sulphide Acids. II. *iso*Butyl Ether of Thioglycollic Acid [*iso*Butylthiolacetic Acid]. Y. UYEDA and J. KAMON (*J. Chem. Soc. Japan*, 1923, **44**, 1061—1070).—iso*Butylthiolacetic acid*, $CHMe_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CO_2H$, a pale yellow liquid, b. p. 244°, d^{25} 1·0685, n^{25} 1·4750, is obtained by boiling a solution of the sodium salt of *iso*butyl mercaptan with sodium chloroacetate. The *strontium* $(+1{\cdot}5H_2O)$, *nickel* $(+2H_2O)$, *cobalt* $(+2H_2O)$, *cadmium* $(+H_2O)$, *copper* $(+2H_2O)$, and *silver* salts are described. It gives a chloride, b. p. 104—105°/13—15 mm., d^{25} 1·1034, n^{25} 1·4780; an *amide*, m. p. 49°; an *ethyl* ester, b. p. 209°, d^{25} 0·9848, n^{25} 1·4550; a *propyl* ester, b. p. 228°, d^{25} 0·9648, n^{25} 1·4550; an iso*butyl* ester,

b. p. 234°, d^{25} 0·9526, n^{25} 1·4530; and a *butyl* ester, b. p. 245°, d^{25} 0·9577, n^{25} 1·4515. K. K.

Catalytic Action. VII. Catalytic Action of Reduced Copper on Acetaldehyde. S. Komatsu and M. Kurata (*Mem. Coll. Sci. Kyoto*, 1924, 7, 293—295).—Acetaldehyde, when passed over reduced copper heated at 300°, is partly converted into crotonaldehyde, paraldehyde, and metaldehyde. F. G. M.

Polymerisation of Aldols. M. Bergmann and E. Kann (*Annalen*, 1924, **438**, 278—293).—*Acetylcycloaldol* (*paraldol di-acetate*), $CH_3 \cdot CH(-O-) \cdot CH_2 \cdot CH \cdot OAc$, b. p. 156—158°/12 mm., n_D^{20} 1·4425, d_4^{20} 1·100, is obtained by the action of cold acetic anhydride on acetaldol in presence of pyridine. It remains associated to the bimolecular form in benzene, phenol, or glacial acetic acid, but the vapour dissociates gradually at 140° and rapidly at 180°. It does not react with methyl orthoformate, but yields a colourless, viscous *oxime*, b. p. 120—122°/12 mm., n_D^{20} 1·4500. Aldoldimethylacetal affords, similarly, *acetylaldoldimethylacetal*, $CHMe(OAc) \cdot CH_2 \cdot CH(OMe)_2$, b. p. 84—86°/13 mm., which is hydrolysed by cold *N*/1-sulphuric acid to *γ-acetoxy*-n-*butaldehyde*, sour-smelling, mobile liquid, b. p. 72—76°/12 mm. The latter reacts with methyl orthoformate, yielding the dimethylacetal again, and forms the same oxime as the above acetyl*cyclo*aldol. The dimethylacetal is also obtained by the action of methyl orthoformate on paraldol. *Hydracetyl-acetone monoacetate*, b. p. 84°/12 mm. (*phenylhydrazone*, hexagonal plates, m. p. 115°); *acetopropyl acetate*, $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OAc$, b. p. 91°/12 mm., n_D^{14} 2·4295, d_4^{14} 1·0186; and *acetobutyl acetate*, b. p. 114—116°/12 mm., $n_D^{13·5}$ 1·4336, $d_4^{13·5}$ 1·002, none of which is associated in solution, are described. γ-Methylglucoside, tetramethyl-γ-methylglucoside, *tetra-acetyl-γ-methylglucoside*, a pale yellow syrup, b. p. 156°/0·3 mm., and tetra-acetyl-β-methylglucoside are unimolecular in solution. The tendency to polymerisation of the aldol *cyclo*acetates is ascribed to the unsaturated affinity of the bridge-oxygen, and is greater the nearer the two carbon atoms thereby connected. F. G. W.

Action of Calcium Hydride on certain Organic Compounds. I. Acetone. C. Porlezza and U. Gatti (*Gazzetta*, 1924, **54**, 491—509).—The condensation of acetone in presence of calcium hydride yields α- and β-*iso*xylitones (cf. Knoevenagel and Blach, A., 1906, i, 964; Knoevenagel and Beer, *ibid.*) and other apparently analogous compounds. In presence of calcium or its oxide, acetone undergoes a condensation which is similar, at least qualitatively, to that effected by the hydride, but the latter acts more energetically in this respect. Under no conditions was it found possible to obtain the compound, b. p. 226—236°, described by Reich and Serpek (A., 1920, i, 249). T. H. P.

Reactions of Chloroacetone 2 : 4-Dinitrophenylhydrazone. C. Bülow and F. Seidel (*Annalen*, 1924, **439**, 48—58).—The con-

densation of chloroacetone with 2 : 4-dinitrophenylhydrazine at first gives *chloroacetone* 2 : 4-*dinitrophenylhydrazone*,

$$(NO_2)_2C_6H_3\cdot NH\cdot N{:}CMe\cdot CH_2Cl,$$

yellow needles, m. p. 124—125·5°. Prolonged boiling in alcoholic solution converts it into the corresponding *osazone*,

$$(NO_2)_2C_6H_3\cdot NH\cdot N{:}CH\cdot CMe{:}N\cdot NH\cdot C_6H_3(NO_2)_2,$$

m. p. 298°. The chlorine atom of the hydrazone has a greatly increased reactivity and reacts with a large number of amines. One mol. of ammonia condenses with 2 mols. of the phenylhydrazone to yield the *imine*, $NH[CH_2\cdot CMe{:}NR]_2$, where R is the hydrazone residue, m. p. 215°, and methylamine yields the corresponding *methylimine*, microscopic yellow needles, m. p. 222°. Camphylamine yields a *camphylimino* derivative, m. p. 184—185°, pyridine a quaternary *pyridinium* salt, $CMe{:}NR\cdot CH_2\cdot NC_5H_5Cl$, greenish-yellow, becoming red at 180—190°, m. p. 201—203°. Piperidine yields a *tertiary base*, m. p. 200° (decomp.), whilst quinoline yields a *compound* analogous to that obtained with pyridine, but which retains 1 mol. of water of crystallisation very tenaciously and is isolated as the *osazone*, m. p. 295° (much decomp.). The action of phenylhydrazine on chloroacetone 2 : 4-dinitrophenylhydrazone yields the *mixed osazone*, carmine-red needles, m. p. 232°. By the action of sodium acetate in alcoholic solution on chloroacetone 2 : 4-dinitrophenylhydrazone, the corresponding *phenylhydrazone* of *acetonyl acetate* (cf. Henry, A., 1873, 379), long, flat, yellow tablets, m. p. 106—107°, is obtained, whilst by the action of potassium thiocyanate the corresponding *thiocyanoacetone* 2 : 4-*dinitrophenylhydrazone*, golden, iridescent crystals, m. p. 127—128°, is formed. By intramolecular rearrangement this compound forms a cyclic *compound*, $\begin{matrix}CH_2\cdot S-C{:}NH\\ |\quad\quad\quad\quad ||\\ CMe{:}N\cdot N\cdot C_6H_3(NO_2)_2\end{matrix}$, which is isolated as its *hydrochloride*. It forms a *chloroaurate*,

$$(C_{10}H_9O_4N_5S)_2,HAuCl_4,HCl.$$

With potassium xanthate in the cold, chloroacetone 2 : 4-dinitrophenylhydrazone forms a *xanthate*, $CMe(:NR)\cdot CH_2\cdot S\cdot CS\cdot OEt$, fine needles, m. p. 77—78° (cf. this vol., i, 573). J. W. B.

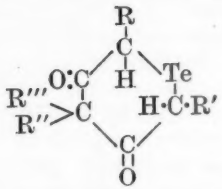
Special Examples of Grignard's Reaction. H. Goudet and H. Paillard.—(See i, 1055.)

Dehydration of some new Pinacones. R. Locquin and L. Leers (*Compt. rend.*, 1924, **178**, 2095—2098).—Dehydration of a series of pinacones, as in the case of those already studied (Meerwein, A., 1913, i, 485; Locquin and Sung, this vol., i, 613), results in formation only of $CRMe_2\cdot CO\cdot Me$ from $CRMe(OH)\cdot CMe_2\cdot OH$; the alternative transformation into $CMe_3\cdot CO\cdot R$ does not appear to occur. This was shown both by oxidation of the resulting ketone to the corresponding acid and by comparison with the latter type of ketone prepared by condensation of pivaloyl chloride with organo-zinc compounds of the type R·Zn·I. The following are described: γγ-*Dimethylhexan*-β-*one*, b. p. 149°/745 mm., d_4^0 0·838, *semicarbazone*, m. p. 119·5°, *oxime*, m. p. 58°, b. p. 100—101°/12 mm.;

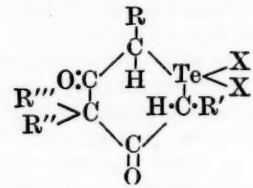
αα-dimethylpentoic acid, b. p. 98—99°/9 mm., *chloride*, b. p. 45°/10 mm., *methyl* ester, b. p. 144—145° ; *βγ-dimethylheptane-βγ-diol*, *γγ-dimethylheptan-β-one*, b. p. 169·5°/735 mm., d_4^{11} 0·834, *semicarbazone*, m. p. 130—131°; *αα-dimethylhexoyl chloride*, b. p. 56°/10 mm., *amide*, m. p. 92°; *ββ-dimethylheptan-γ-one*, b. p. 164°/735 mm., d_4^{11} 0·823, *semicarbazone*, m. p. 142—143°; *γγ-dimethyloctan-β-one*, b. p. 75°/10 mm., d_4^{0} 0·843, *semicarbazone*, m. p. 106°; *αα-dimethylheptoic* acid, b. p. 130°/12 mm., *chloride*, b. p. 74—75°/10 mm., *amide*, m. p. 101—102°; *ββ-dimethyloctan-γ-one*, b. p. 72°/10 mm., d_4^{0} 0·834, *semicarbazone*, m. p. 139—140°. H. J. E.

***cyclo*Telluropentanediones and *cyclo*Telluripentanedione Dihalides.** G. T. MORGAN and H. D. K. DREW (*J. Chem. Soc.*, 1924, **125**, 1601—1607).—The behaviour of a series of tellurium β-diketones towards hydroxylamine shows that these compounds are diketonic in structure, since they yield dioximes as well as monoximes. It is concluded that the cyclic tellurium β-diketones and their corresponding dihalides belong to two new types of cyclic organometalloidal compounds, that represented by (I) being

(I.)



(II.)



designated cyclo*telluropentane*-3 : 5-*diones* and (II) cyclo*telluripentane*-3 : 5-*dione*-1 : 1-*dihalides*; X may be Cl, Br, or I, and R, R′, etc. may stand for hydrogen atoms or similar or dissimilar alkyl or arylalkyl (*e.g.*, benzyl) groups, but not for phenyl or other purely aromatic groups. cyclo*Telluri*-4 : 4-*dimethylpentane*-3 : 5-*dione*-1 : 1-*dichloride*, m. p. 194°, prepared by refluxing a chloroform solution of dimethylacetylacetone with tellurium tetrachloride, was converted by aqueous potassium metabisulphite into cyclo*telluro*-4 : 4-*dimethylpentane*-3 : 5-*dione*, m. p. 124—125°. Oximation of tellurium acetylacetone gave cyclo*telluropentane*-3 : 5-*dionedioxime*, m. p. indefinite; similarly, tellurium ethyl acetylacetone yielded cyclo*telluro*-4-*ethylpentane*-3 : 5-*dionedioxime* (decomp. 192° after darkening at 173°). Steric hindrance manifests itself as substitution proceeds, monoximes being formed when oximation is conducted in presence of dilute acetic acid, and dioximes under more drastic conditions in alkaline solution. cyclo*Telluro*-4 : 4-*dimethylpentane*-3 : 5-*dione*-5-*monoxime* has m. p. 183—184° or 180° when crystallised from benzene or alcohol, respectively; the corresponding *dioxime* decomposes at 235°. cyclo*Telluro*-2 : 4-*dimethylpentane*-3 : 5-*dione*-5-*monoxime* and the corresponding *dioxime* decompose respectively at 168° and 198°.

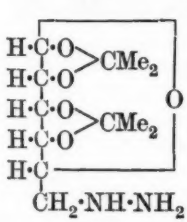
Derivatives of tellurium *n*-butyrylacetone exhibit isomerism of the Hantzsch–Werner type and two isomeric dioximes have been isolated which are provisionally designated as α- and β-forms, and

may have respectively the *syn*- and *anti*-configurations. α-cyclo-*Telluro*-2-*ethylpentane*-3 : 5-*dionedioxime*, m. p. 149°, and its β-*isomeride*, m. p. 183°, are produced in the ratio of 5 : 1 by oximation in alkaline solution.

Three dynamic isomerides of β-diketones exist as evidenced by the interaction of acetylacetone and its homologues with metallic compounds and selenium and tellurium tetrachlorides. (1) A *trans*-monoenolic form reacts in the case of the formation of derivatives of Cu, B, Si, Ge, Ti, Sn, and Zr. (2) A *cis*-monoenolic form takes part in condensation with $SeCl_4$. (3) A diketonic form interacts with $TeCl_4$ to form a six-membered ring in which enolisation can only occur under conditions of strain tending to disrupt the ring. C. J. S.

The Anthocyanin Pigment of *Ipomœa hederacea*. Y. YAMAGUCHI (*Ber. deut. bot. Ges.*, 1924, **42**, 144—147).—The anthocyanin was extracted from the flowers of *Ipomœa hederacea* by treatment with methyl alcohol containing 3% of hydrochloric acid and precipitated with ether. A very small yield of reddish-brown, rhombic crystals was obtained by mixing the crude product with 1% hydrochloric acid and a large volume of 1·5% picric acid solution at 50° and allowing to stand for 2 months. The anthocyanin is tentatively named hederacein. The sugar obtained on acid hydrolysis of the crude product and removal of the anthocyanidin was almost certainly dextrose and not galactose. C. T. G.

Nitrogenous Derivative of Diacetoneglucose. E. MERCK CHEMISCHE FABRIK (D.R.-P. 382913; from *Chem. Zentr.*, 1924, i, 1591).—*Hydrazinediacetoneglucose* (annexed formula), from toluene-*p*-sulphonyldextrosediacetone and hydrazine, has m. p. 96—97°, $[\alpha]_D$ +83°. It forms an *iso*propylidene *compound*, and a benzylidene *compound*, m. p. 99—100°, $[\alpha]_D$ +144° in *s*-tetrachloroethane. G. W. R.

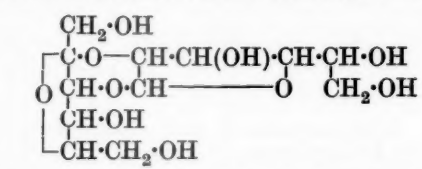


Mechanism of the Oxidation of Lævulose in Phosphate Solutions. O. MEYERHOF and K. MATSUOKA (*Biochem. Z.*, 1924, **150**, 1—11).—The spontaneous oxidation of lævulose in concentrated phosphate solutions, described by Warburg and Yabusoe (this vol., i, 713), is shown to be due to the catalytic action of a metal, since the reaction is inhibited by the presence of potassium cyanide and of sodium pyrophosphate, which would lead to the formation of stable complex salts; it is accelerated by the addition of copper, iron, and manganese, this acceleration being abolished by the simultaneous addition of cyanide, and it takes place equally well in solutions of arsenates. C. R. H.

Action of Heat on Sucrose. A. PICTET and N. ANDRIANOFF (*Helv. Chim. Acta*, 1924, **7**, 703—707; cf. this vol., i, 499).—When sucrose (m. p. 183°) is heated at 185—190°/10—15 mm. until it has lost 5% of its weight, iso*saccharosan*, $C_{12}H_{20}O_{10}$, is obtained, which, when precipitated from methyl-alcoholic solution by addition

of acetone, forms a white, hygroscopic, amorphous powder with a bitter taste, m. p. 94—94·5°, $[\alpha]_D^{22}$ +64·0°; it rapidly undergoes hydrolysis to dextrose and lævulose in aqueous solution. The *hexa-acetate* forms colourless prisms, m. p. 79—80°. If the heating be continued until the sucrose has lost 10% of its weight, caramelan, $C_{24}H_{36}O_8$ (cf. Cunningham and Dorée, A., 1917, i, 513), is obtained as a pale yellow, hygroscopic, amorphous substance, much purer than when produced in an open vessel. It has m. p. 144—145°, $[\alpha]_D^{22}$ +80·0°. Further heating of sucrose, until 15% of the weight has been driven off, leaves caramelen, $C_{36}H_{50}O_{25}$, a brown, non-hygroscopic powder, m. p. 204—205°, $[\alpha]_D^{23}$ +65·4°. W. A. S.

Constitution and Synthesis of *iso*Saccharosan. A. Pictet and P. Stricker (*Helv. Chim. Acta*, 1924, **7**, 708—713).—*iso*Saccharosan (cf. preceding abstract) reduces Fehling's solution to half the extent that it should do if the reduction depended on hydrolysis to a mixture of dextrose and lævulose. Moreover, *iso*saccharosan yields an *osazone*, $C_{24}H_{32}O_9N_4$, m. p. 124—125°, in addition to glucosazone, which is the chief product of the reaction. These results indicate that the substance is not a simple anhydride of sucrose, a constitution for which would be difficult to frame. Sucrose is converted at its melting point without loss of weight (cf. Gelis, *Ann. Chim.*, 1859, [iii], **57**, 234) into a mixture of dextrose and lævulosan; in accordance with this it is found that *iso*saccharosan is formed when a mixture of lævulosan and dextrose is heated at 185°/15 mm. until 5% of the total weight is lost. Likewise, if a mixture of glucosan and lævulosan be similarly heated, *iso*saccharosan is formed, no loss of weight taking place in this case. To *iso*saccharosan is attributed the constitution:



Preliminary experiments indicated that by treating *iso*saccharosan with cold 5% ammonia, *iso*sucrose could be obtained. W. A. S.

Glycogen. I. Partial Methylation, and the Isolation of Methylated Glucoses. A. K. Macbeth and J. Mackay (*J. Chem. Soc.*, 1924, **125**, 1513—1521).—Glycogen was alkylated by the repeated action of methyl sulphate in the presence of sodium hydroxide. After three methylations, the product contained 26·7% OMe. Methyl alcohol was then used to keep the product in solution, whereby ultimately a compound with more than 36·4% OMe, corresponding with an introduction of 2—3 methyl groups for each glucose residue, was isolated. Either steric hindrance or physical condition hinders further alkylation. A product containing 36·4% OMe had $[\alpha]_D$ +179·83° in chloroform. Hydrolysis with methyl-alcoholic hydrogen chloride yielded (*a*) almost pure tri-

methyl methylglucoside, which on treatment with methyl iodide and silver oxide was converted into 2 : 3 : 5 : 6-tetramethyl methylglucoside and therefore contained the butylene oxide linking. Hydrolysis with 6% hydrochloric acid changed it to 2 : 3 : 6-trimethylglucose with constants in good agreement with those of the crystalline 2 : 3 : 6-trimethylglucose from cellobiose, cellulose, and starch; (*b*) a dimethyl methylglucoside belonging to the butylene oxide series which was hydrolysed to a dimethylglucose differing from the 2 : 3-compound described by Irvine and Scott (T., 1913, **103**, 575) and possibly a 2 : 5-derivative, and (*c*) a probable mixture of mono- and di-methyl methylglucosides. It was possible to use glycogen possessing a fairly high nitrogen content in the above methylations; the nitrogen disappeared in the early stages and the products did not differ from those in which rigorously purified material was used. The close agreement between starch and glycogen on methylation and the similarity of the products on hydrolysis, indicates that the polysaccharides are built up from the same basal unit, and that the various formulæ proposed for starch may also be applied to glycogen. A. C.

Redetermination of the Heat of Combustion of Glycogen with Special Reference to its Physiological Importance. W. K. Slater (*Biochem. J.*, 1924, **18**, 621—631).—The heat of combustion of glycogen monohydrate in dilute solution is 3836 cals. per gram. S. S. Z.

Cellulose Nitrate and Camphor. J. B. Nichols.—(See i, 972.)

Soluble Cellulose Esters of Higher Ethylenic Fatty Acids. H. Gault and [Mlle.] M. Urban (*Compt. rend.*, 1924, **179**, 333—334).—In continuation of previous work (cf. Gault and Ehrmann, A., 1923, i, 757), *cellulose triundecylenate*, m. p. (indef.) above 190°, has been prepared by allowing undecylenyl chloride to act, in toluene, on hydrocellulose, previously saturated with a mixture of toluene and excess of pyridine, at 110—120° for 2 hours. The ester is hydrolysed only with great difficulty, and it is therefore not possible to determine the corresponding acid in this manner. J. W. B.

A Substance giving a Blue Colour with Iodine in the Asci of Lichens (*iso*Lichenin). H. Ziegenspeck (*Ber. deut. bot. Ges.*, 1924, **42**, 116—119).—A compound, giving a blue coloration with iodine, to which the name iso*lichenin* is given, has been isolated from an extract of the apothecia of the lichen *Xanthoria parietina* and also from other species. It is a carbohydrate, related to starch, stable towards diastase, and giving dextrose and a little methylpentose on complete hydrolysis with sulphuric acid. It has been detected in the vegetative thallus of only one species—*Cetraria islandica*; in the hymenium of several, and in the young asci of a large number of species. It occurs in the asci until they are almost fully developed, but disappears with the development of the spores, being converted into glycogen. *iso*Lichenin is considered to have the function of a reserve food material. C. T. G.

Hydrocellulose. H. GAULT and B. C. MUKERJI (*Compt. rend.*, 1924, **179**, 402—405).—The formation of hydrocellulose by the action of dilute sulphuric acid on cellulose has been studied systematically, the increase in the copper number, determined by the method previously described (this vol., ii, 280), giving a measure of the degradation. The rate of formation of hydrocellulose varies directly with the strength of the acid, the time and temperature of immersion, and the temperature of drying. With 5% sulphuric acid, the degradation begins to be appreciable only at 70°. Hauser and Herzfeld's observation (A., 1915, i, 941) that the copper number of hydrocellulose falls to that of pure cellulose on prolonged extraction with boiling water was not confirmed. R. B.

Action of Aqueous Sulphurous Acid on Lignocellulose. C. F. CROSS and A. ENGELSTAD (*J. Soc. Chem. Ind.*, 1924, **43**, 253—257T).—The process for the manufacture of cellulose from wood by digestion with a 7% solution of sulphurous acid, free from sulphuric acid (Brit. Pat. 202016, 1922), proves that sulphonation is a direct reaction of sulphurous acid with certain groups of the lignone complex. The secondary effects which differentiate the products of the sulphurous acid process from those of the bisulphite process are the degree of sulphonation, deoxidation of CO groups, and condensation of the sulphonated complex. Analogous reactions are observed with cinnamaldehyde under the same treatment, but not with benzaldehyde or dextrose. Dextrose, however, is partly broken down with formation of acetic acid and caramel, whilst elementary sulphur and sulphur-oxygen by-products are detected. Digestion of oil of turpentine with aqueous sulphurous acid also forms small quantities of sulphur. Digestion of cotton cellulose with pure aqueous sulphurous acid leads to a pronounced degradation of the cellulose, indicating the necessity for synchronising the exposure of the wood cellulose by removal of lignone with the substantial exhaustion of the free sulphurous acid in the digestion liquor. One of the characteristic features of this process is the production of sulphuric acid as the result of deoxidation of certain groups of the lignone, and the conditions have been studied for limiting this phase of the reaction. Chemical attack on the cellulose is considerably promoted by fine subdivision of the raw material without a corresponding intensification of the reaction with the lignone. J. F. B.

Lignosulphonic Acid obtained by the Action of Sulphurous Acid on Spruce Wood. C. DORÉE and L. HALL (*J. Soc. Chem. Ind.*, 1924, **43**, 257—263T).—The liquor obtained by digestion of wood with free sulphurous acid differs from that of the ordinary digestion with calcium hydrogen sulphite in its lower degree of sulphonation, its tanning qualities, and its capacity to form gels, these pronounced colloid qualities being associated with the lower temperature of digestion, viz., 100—110°. The lignosulphonic acid has been separated by prolonged dialysis and contains only 5·5% of sulphur as against 7·3% for the bisulphite product. Its empirical formula is $C_{26}H_{30}O_{12}S$, and according to its reactions with α-naphthylamine

it consists practically entirely of a substance of Klason's α (aldehydic) type of lignone. The characterised groups in this complex are summarised in the expression

$$C_{21}H_{15}O_2(SO_3H)(OH)_2(CH_2{\cdot}OH)(CH{\cdot}OH)(CHO)(OMe)_2.$$

On heating with 5% nitric acid, these groups are respectively changed with the following result,

$$C_{22}H_{22}O_5(NO_2)_2(OH)_3(CO)(CO_2H)(CO_2H)(OMe),$$

the nature of the modification of the changed methoxyl group being unexplained. The reactions of this nitro compound on reduction, giving with loss of ammonia a nitrogen-free ketone with three CO groups, show no analogy with the aromatic type and the behaviour of the system generally recalls that of certain unsaturated terpenes of the cholesterol series. Further oxidation by 32% nitric acid gives oxalic acid and a substantial yield of an acid, $C_{20}H_{24}O_{12}(CO_2H)_6(NO_2)_2$. The persistence of the C_{26} complex through all these reactions with a resistant nucleus of the order of C_{20} suggests that the nucleus of lignone is hydroaromatic in character, consisting of a complex of reduced rings somewhat resembling the reduced benzophenanthrene hydrocarbon formulated by Schrauth (A., 1923, i, 443). This involves the general absence of oxygen linkings, the direct attachment of the side groups, including the CHO group, to the carbon atoms of the ring, and the presence of double linkings in the reduced ring. J. F. B.

Preparation of αβγ-Triaminopropane and Formation of Complex Metallic Derivatives. W. J. Pope and F. G. Mann (*Compt. rend.*, 1924, **178**, 2085—2086; cf. Curtis and Hesse, A., 1901, i, 70).—From citric acid the following substances were successively prepared: Acetonedicarboxylic acid, di*iso*nitrosoacetone, diaminoacetone, diacetyldiaminoacetoxime, *αβγ-triaminopropane*. The yield at each stage is stated to be satisfactory. The base is converted into *cobaltiditriaminopropane chloride* and *rhodiditriaminopropane chloride*. H. J. E.

Preparation of a Derivative of Hexamethylenetetramine. R. Wolffenstein (D.R.-P. 382904; from *Chem. Zentr.*, 1924, i, 968).—*Hexamethylenetetramine formate* is crystalline and has m. p. about 60°. G. W. R.

Synthesis of Hydroxyamines by the Curtius Method. P. A. Levene and J. Scheidegger (*J. Biol. Chem.*, 1924, **60**, 179—181).—Ethyl β-hydroxybutyrate is converted successively into *β-hydroxybutyrihydrazide*, m. p. 119—120°, β-hydroxybutyrazide, and *di-β-hydroxypropylacetamide* (*picrate*, m. p. 118—119°). The latter is hydrolysed to β-hydroxypropylamine (*chloroplatinate*, m. p. 210° after softening at 205°). C. T. G.

Formation of Bismuthamines. A. C. Vournazos (*Compt. rend.*, 1924, **178**, 2089—2092).—A brief description of a series of bismuthamines (cf. A., 1923, i, 759) with their formulæ; these substances have been prepared by combination of halides of tervalent bismuth with salts of ammonium, of various types of amines and of alkaloids. Bismuth nitrate and sulphate also yield similar

products. The co-ordination number of the bismuthomonoamines is 4, whilst that of the triamines is 6. The compounds resulting from the action of a bismuth halide, BiX_3, on an amine salt, RNH_3Z, are identical with those derived from BiZ_3 and RNH_3X if the affinity of bismuth for X is greater than that for Z. H. J. E.

N-Alkylamino Fatty Acids and their N-Acyl Derivatives. H. SCHEIBLER (D.R.-P. 386743; from *Chem. Zentr.*, 1924, i, 1592—1593; cf. Scheibler and Baumgarten, A., 1922, i, 655).—The following new compounds are mentioned: *ethyl cyanobenzyl-α-aminopropionate*; *benzylidenealanine*; *N-benzylalanine hydrochloride*, m. p. 258°. G. W. R.

Chain-forming Reactions of the Amides of α-Hydroxy-acids. A. SCHMUCK (*Biochem. Z.*, 1924, **147**, 193—202).—The amides of glycollic and lactic acids, obtained by treating the corresponding cyclic anhydrides with ammonia, yield, when heated in a stream of ammonia at 160—200°, *amidides* or *oxyamidides*, $OH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NH_2$, hygroscopic crystals, m. p. 86°, and $CHMe(OH){\cdot}CO{\cdot}NH{\cdot}CHMe{\cdot}CO{\cdot}NH_2$, small, hygroscopic tables, m. p. 52°, respectively, which give the biuret and alkaloidal precipitation reactions and are closely related to peptides. The compound thus prepared from lactamide yields on hydrolysis with 5% hydrochloric acid, alanine and lactic acid. In the case of glycollamide, the yield of amidide is small, and an amorphous substance, $C_4H_6O_2N_2$, containing 3·77% of amide nitrogen, is also obtained. J. P.

Relation between Crystal Structure and Constitution of Carbon Compounds. II. Crystallography of further Simple Substitution Products of Methane. I. E. KNAGGS (*J. Chem. Soc.*, 1924, **125**, 1441—1444).—A crystallographic description is given of chlorobromoacetomethylamide, chlorobromoacetoethylamide, dichloroacetoethylamide, dichloroacetomethylanilide, and dichloroacetoethylanilide (cf. McKie, this vol., i, 715). S. B.

Action of Hydroxylamine on Ethyl Tartrate. A. J. A. GUILLAUMIN (*Compt. rend.*, 1924, **178**, 1986—1988).—An alcoholic solution of ethyl tartrate (½ mol.) to which hydroxylamine (2 mols.) has been added, when kept at the ordinary temperature, deposits crystals of *tartramhydroxamic acid*, $CO(NH_2){\cdot}[CH{\cdot}OH]_2{\cdot}C(OH){:}N{\cdot}OH$, m. p. 170—172° (decomp.), $[\alpha]_D^{18}$ 96° 30′, *tetra-acetyl* derivative, m. p. 105°, *tribenzoyl* derivative, m. p. 203°. The substance exhibits mutarotation and, unlike other hydroxamic acids, forms no precipitate with copper acetate; further, ferric chloride gives with it a red coloration on standing. The structure is thus probably of the type $R{\cdot}CO{\cdot}NH{\cdot}OH$, which is rearranged as above on solution in water. H. J. E.

Heat of Formation of Calcium Cyanamide. N. KAMEYANA (*J. Faculty Eng., Tokyo Imp. Univ.*, 1923, **13**, 61—71).—The author criticises the calculations of the heat of formation of calcium cyanamide given by Thompson and Lombard (*Met. Chem. Eng.*, 1910, **8**, 682) and Dolch (A., 1921, ii, 17). E. M. C.

Behaviour of Calcium Cyanamide when Heated in Nitrogen at High Temperatures. N. KAMEYANA (*J. Faculty Eng., Tokyo Imp. Univ.*, 1923, **13**, 75—102).—On heating calcium cyanamide in nitrogen to temperatures above 1250°, considerable loss occurred with evolution of nitrogen and severe corrosion of the porcelain reaction tube over a considerable distance. It is suggested that the calcium cyanamide sublimed at this temperature and that the vapour reacted with the porcelain. E. M. C.

Preparation of Guanidinium Salts from Calcium Cyanamide. J. S. BLAIR and J. M. BRAHAM (*Ind. Eng. Chem.*, 1924, **16**, 848—852).—A cold, filtered, aqueous extract of calcium cyanamide is neutralised with sulphuric acid, and evaporated below 80° to a cyanamide content of 165 g. per l. Ammonium nitrate (2 mols. per mol. of cyanamide) is added, and the solution heated slowly to 155°, this temperature being maintained for 3 hours. The hot solution is filtered, the guanidine nitrate crystallising on cooling the filtrate. About 80% of the cyanamide is converted into guanidine. [Cf. *B.*, 1924, 806.] F. G. W.

Peralkylated Guanidines. II. H. LECHER and F. GRAF (*Annalen*, 1924, **438**, 154—169; cf. A., 1923, i, 761).—Pentamethylguanidine combines with ethyl iodide in ether solution to form *pentamethylethylguanidinium iodide*, colourless crystals, which unites with iodine to produce the corresponding *tri-iodide*, m. p. 58—59°. NNS-*Trimethyl*-N′-*ethyl*-ψ-*thiocarbamide*, $NMe_2 \cdot C(:NEt) \cdot S \cdot Me$, an oil, b. p. 69·2—69·5°/12 mm., is obtained by treating *NN*-dimethyl-*N*′-ethylthiocarbamide (Billeter, A., 1893, i, 575) with methyl sulphate; when it is heated at 100° with dimethylamine in presence of mercuric chloride, NNN′N′-*tetramethyl*-N″-*ethylguanidine*, an oil, b. p. 55·5°/11 mm., is obtained. The latter combines with methyl iodide to give the same pentamethylethylguanidinium iodide as before; addition therefore takes place in both cases at the imino group, and presumably salt-formation takes place in the same way, not, as hitherto supposed, at one of the amino groups.

Guanidinium iodide, prepared by dissolving the carbonate in hydriodic acid, does not form a tri-iodide. *Pentamethylguanidinium* and *hexamethylguanidinium iodides* were obtained in a similar way; the latter yields a *tri-iodide*, red leaflets, m. p. 118—120°. *Hexamethylguanidinium hydroxide* can be obtained only in aqueous solution, best by treating the iodide with thallium sulphate and the resulting sulphate with barium hydroxide. A dilute solution is tolerably stable, but decomposition takes place when it is boiled alone or when sodium hydroxide is present, or even when it is concentrated under diminished pressure, the products of the decomposition being tetramethylcarbamide and dimethylamine.

Guanidinium hydroxide and its alkyl derivatives are bases comparable in strength with the alkali hydroxides. Pentamethylguanidinium hydroxide precipitates from solutions of their salts the hydroxides of the alkaline-earth and heavy metals. W. A. S.

Constitution of Thiocarbamide and "Thiuronium" Salts. H. LECHER and C. HEUCK (*Annalen*, 1924, **438**, 169—184).—It is

suggested that the salts of carbamide and of thiocarbamide be termed "uronium" and "thiuronium" salts, respectively. When thiocarbamide forms a salt, the hydrogen of the acid attaches itself to the sulphur atom because pentamethylthiuronium iodide (tetramethylthiocarbamide methiodide, Delépine, A., 1911, i, 23) may be obtained by combining with methyl iodide either *NNN'N'*-tetramethylthiocarbamide or *NNN'S*-tetramethyl-ψ-thiocarbamide. In the first case, reaction proceeds rapidly in ethereal solution; in the second, the two reagents were mixed without a solvent, as it was found that in ethereal solution only 10% of the product had separated after two days. The two products were proved to be identical by converting them into the corresponding *picrate*, m. p. 92—93·5°.

NN-Dimethylthiocarbamyl chloride (Billeter, A., 1893, i, 575) interacts with diethylamine in hot benzene to yield NN-*dimethyl*-N'N'-*diethylthiocarbamide*, an oil, b. p. 119—120°/10 mm. Methylthiocarbimide and diethylamine unite in aqueous suspension to form N-*methyl*-N'N'-*diethylthiocarbamide*, $NHMe{\cdot}CS{\cdot}NEt_2$, m. p. 36—37·5°; when the latter is treated in hot methyl alcohol with methyl sulphate, NS-*dimethyl*-N'N'-*diethyl*-ψ-*thiocarbamide*, $NMe{:}C(SMe){\cdot}NEt_2$, an oil, b. p. 79—80°/10—11 mm., is obtained. When *NN*-dimethyl-*N'N'*-diethylthiocarbamide or *NS*-dimethyl-*N'N'*-diethyl-ψ-thiocarbamide is treated with methyl iodide, or when *NNS*-trimethyl-*N'*-ethyl-ψ-thiocarbamide is treated with ethyl iodide, NNS-*trimethyl*-N'N'-*diethylthiuronium iodide*, $SMe{\cdot}C(NEt_2){:}NMe_2I$, m. p. 94—95°, is obtained. The three products were conclusively proved to be identical by preparing from each the corresponding *picrate*, m. p. 80—83°. These results need further investigation. Pentamethylthiuronium hydroxide solutions, obtained by treating the iodide with sodium hydroxide, decompose even at room temperature, tetramethylcarbamide and methyl mercaptan being formed. The base was found to be comparable in strength with the alkali hydroxides. W. A. S.

Chemical Behaviour of α- and β-Hydroformamine Cyanides (Methyleneaminoacetonitriles). H. W. Rinehart and T. B. Johnson (*J. Amer. Chem. Soc.*, 1924, **46**, 1653—1661; cf. this vol., i, 625).—Although α-hydroformamine cyanide, m. p. 129°, yields the hydrochloride of ethyl aminoacetate on hydrolysis with alcoholic hydrogen chloride (Jay and Curtius, A., 1894, i, 162; 1899, i, 9; Klages, A., 1902, i, 354), the β-compound, m. p. 86°, merely decomposes to ammonium chloride and a nitrogen derivative of unknown constitution. When hydrolysed in alkaline solution the α-isomeride yields ammonia equivalent to one-half of its nitrogen, whilst the β-compound readily gives off two-thirds of its nitrogen as ammonia. Hydrolysis is less ready with sulphuric acid and the amount of ammonia produced is less, but, in the case of the β-isomeride, increases with the concentration of the acid. Both isomerides are slowly hydrolysed in boiling aqueous solution, the α-compound giving off ammonia rapidly at first, but the rate of production rapidly falls off, whilst the β-compound gives off

ammonia slowly at a nearly constant rate up to 17% of its nitrogen, as compared with 40% for the α-isomeride. α-Hydroformamine cyanide yields with hydrogen sulphide and alcoholic ammonia a white, crystalline *substance*, $C_8H_{12}N_5 \cdot CS \cdot NH_2$, m. p. 152—153° on rapid heating, 125—140° (decomp.) in the ordinary way, prolonged treatment giving dithiopiperazine or a thiopolypeptide. β-Hydroformamine cyanide similarly yields a colourless, crystalline *substance*, $C_7H_{12}N_4(CS \cdot NH_2)_2$, m. p. 148° (decomp.). An examination of the absorption spectra of the two isomerides in acetone solution supports the view that neither substance contains free ethylenic linkings. R. B.

Butenonitriles. IV. P. Bruylants (*Bull. Soc. chim. Belg.*, 1924, **33**, 331—338).—During the preparation of vinylacetonitrile by the interaction of allyl bromide and cuprous cyanide (A., 1922, i, 817, 924), diallyl is sometimes produced, but the cause is unknown. Vinylacetonitrile is converted into an equilibrium mixture of crotono- and *iso*crotono-nitriles by sodium phenoxide in the presence of phenol, and by aliphatic mono- and di-amines, but not by acidic reagents. Aqueous *N*/10-sodium hydroxide solution also converts vinylacetonitrile into a mixture of the two crotononitriles and some crotonamide, whereas *N*/2 ethyl-alcoholic sodium hydroxide transforms it almost quantitatively into β-ethoxybutyronitrile, whilst an *N*/4-sodium hydroxide solution in alcohol–water (3 : 1 by vol.) gives a mixture of the two isomeric crotononitriles and β-ethoxybutyronitrile. Vinylacetonitrile, when treated with 1 mol. of sulphuric acid, gives a 50% yield of vinylacetic acid, b. p. 72·6—72·8°/13 mm., 169—169·2°/764·3 mm., m. p. −38·2°, d_4^{20} 1·0091, n_D^{20} 1·4252, together with traces of crotonic acid and amide; the vinylacetic acid is identified by conversion into βγ-dibromobutyric acid, and by the close similarity of its absorption spectrum curve with that of vinylacetonitrile. Vinylacetic acid when heated under reflux for 24 hours is converted into crotonic acid, which probably contains some *iso*crotonic acid. Sodium vinylacetate is stable in aqueous solution, but in sodium hydroxide solution is partly converted into sodium crotonate. Both isomeric crotononitriles are converted by concentrated sulphuric acid into the same (solid) crotonic acid. F. G. M.

Phase Rule Study of the Cupro-, Argento-, Auro-, and Thallo-cyanides of Potassium. H. Bassett and A. S. Corbet (*J. Chem. Soc.*, 1924, **125**, 1660—1675).—The curves obtained for the system KCN–CuCN–H_2O at 25° indicate the existence of four complex cyanides, and these have been isolated. $KCu_2(CN)_3,H_2O$, monoclinic scales, was prepared in small quantity by boiling an excess of cuprous cyanide with 10% aqueous solution of potassium cyanide; on concentrating the mother-liquor, there were first deposited crystals (hexagonal plates or needles) of $KCu(CN)_2$, and, later, prismatic crystals of $K_3Cu(CN)_4$. Colourless rhombohedral crystals of the compound $K_3Cu(CN)_4,H_2O$ were obtained by evaporating a solution containing potassium and cuprous cyanides in the molecular ratio of 3 : 1.

In the system KCN–AgCN–H_2O at 25°, the compounds $KAg(CN)_2$, $K_3Ag(CN)_4,H_2O$, and $KAg_2(CN)_3,H_2O$ can exist in contact with the solution. The *complex*, $K_3Ag(CN)_4,H_2O$, was obtained as large, colourless, tabular prisms on evaporating a solution containing potassium and silver cyanides in the ratio 3 : 1. The *salt*, $KAg_2(CN)_3,H_2O$, forms minute needles.

No evidence was obtained for the existence of potassium aurocyanides other than $KAu(CN)_2$. One thallocyanide, $KTl(CN)_2,H_2O$ (rectangular prisms), is capable of existence in the system KCN–TlCN–H_2O. C. J. S.

Decomposition of the Octacyanides of Quadrivalent Molybdenum and Tungsten by Sunlight. I. O. Collenberg (*Z. anorg. Chem.*, 1924, **136**, 245—251).—Sulphuric acid solutions of compounds of the type $K_4R(CN)_8$, where R=Mo or W, are pale yellow in colour, but, on exposure to bright sunlight, they turn, in succession, reddish-brown, dark brown, and eventually green, whilst a brown, flocculent precipitate forms. No definite compounds could be isolated from the decomposed solution. The corresponding octacyanides in *N*-potassium hydroxide solution undergo a change on exposure to bright sunlight involving the replacement of four cyano groups successively by hydroxyl, and the colour of the solution passes through brown to violet. From the violet solutions addition of excess of potassium hydroxide precipitates, in the cold, crystalline substances having the composition

$$K_4[R(OH)_3(CN)_5],xH_2O.$$

The tungsten compound is yellowish-brown in colour and gives violet solutions. The molybdenum compound exists in two forms, one, yellow-brown in colour, crystallising from hot solutions, and the other, reddish-violet in colour, from cold; both give deep blue solutions in water. A. R. P.

Preparation of Hydroxyethylarsinic Acid. Les Établ. Poulenc Frères and C. Oechslin (Brit. Pat. 206143).—An ethylene dihalide is heated with an aqueous solution of an alkali arsenite; the resulting mixture is neutralised with hydrochloric acid and hydrogen peroxide is added to convert any free arsenious into arsenic acid, which is removed with magnesium oxide. W. T. K. B.

Preparation of Magnesium Methyl Chloride for the Grignard Reaction. H. Schmalfuss (*J. pr. Chem.*, 1924, [ii], **108**, 88—90).—The reaction between magnesium and gaseous methyl chloride is greatly accelerated by a catalyst formed by mixing in a flask the magnesium, some ethyl bromide, a few crystals of iodine, and a very little ether. The catalyst is formed at once, dry ether is added, and a stream of dry methyl chloride gas is passed into the boiling ether as fast as it can be absorbed. Using the magnesium methyl chloride thus prepared, 98% of the theoretical yield of diphenylmethylcarbinol was obtained from benzophenone. E. H. R.

Valency Requirements of Organic Radicals. K. VON AUWERS (*Ber.*, 1924, **57**, [*B*], 1051—1056).—A theoretical survey of results obtained by Meerwein (A., 1920, i, 2; this vol., i, 188, 191), von Braun (A., 1923, i, 1193; this vol., i, 632), Skraup (A., 1919, i, 598), Steinkopf (A., 1922, i, 994), and Schonberg (this vol., i, 520) in relation to observations of the author and Zincke on ψ-phenols (A., 1900, i, 159), *p*-hydroxybenzylpiperidines (A., 1906, i, 258), phenyl benzyl ethers (A., 1900, i, 168; 1902, i, 212; 1906, i, 347; 1907, i, 1033), *o*- and *p*-hydroxybenzyl bromides (A., 1900, i, 154), and *pp'*-dihydroxydiphenylmethanes (A., 1906, i, 263; 1907, i, 919). The relative tenacity of the radicals is not under all conditions a measure of their valency requirements, since other factors, such as steric hindrance and ionisation, may come into play. R. B.

Isomerisation due to the Action of Zinc Dust and Alcohol on the Stereoisomeric Dibromodimethyl*cyclo*hexanes. A. USPENSKI (*Trans. Inst. Chem. Reagents, Moscow*, 1923, No. 2, 5—9).—When the solid *cis*-3 : 5-dibromo-1 : 1-dimethyl*cyclo*hexane (A., 1923, i, 666) is reduced by means of zinc dust and alcohol, the product is the pure bicyclic hydrocarbon (*loc. cit.*), b. p. 114—114·1°/740 mm., d_4^{20} 0·8131, n_D^{20} 1·4350; if the liquid isomeride, consisting mainly of the *trans*-form, is employed a mixture is obtained, b. p. 115·5°/740 mm., d_4^{20} 0·7885, n_D^{20} 1·4337, which contains only small quantities of the above hydrocarbon, the greater part consisting of the unsaturated isomeride, as evidenced by the high molecular refractivity and its reaction with permanganate. G. A. R. K.

Refractive Index of Benzene and Carbon Tetrachloride in an Electric Field. PAUTHENIER.—(See ii, 582.)

Sulphonation of Benzene. A. W. HARVEY and G. STEGEMAN (*Ind. Eng. Chem.*, 1924, **16**, 842—845).—When benzene vapour is passed through sulphuric acid (93·2%) at 130—170°, the concentration of the sulphuric acid falls, first rapidly, then more slowly, until a limiting value (0·6% at 170°) is reached. The concentration of benzenesulphonic acid shows a corresponding increase, but reaches a maximum (88—92%) before the limiting sulphuric acid concentration is attained. This point corresponds with the commencement of the formation of diphenylsulphone, according to the equations $2PhSO_3H=Ph_2SO_2+H_2SO_4$, and $PhSO_3H+C_6H_6=Ph_2SO_2+H_2O$. As the sulphone does not appear until the concentration of sulphuric acid has fallen below 10%, its production by the direct action of benzene on sulphuric acid appears to be excluded. F. G. W.

Special Examples of Grignard's Reaction. H. GOUDET and H. PAILLARD (*Helv. Chim. Acta*, 1924, **7**, 638—640).—β-Phthalimidoethyl bromide (ω-bromoethylphthalimide) interacts with magnesium phenyl bromide to form a compound which when treated with water yields 3-*hydroxy*-3-*phenyl*-2-β-*bromoethyl*iso*indolinone*, colourless needles, m. p. 179·5—180·5°. This product will not react further with a Grignard reagent (cf. Sachs and Ludwig, A., 1904, i, 266), nor will the intermediate magnesium

complex interact with magnesium. The magnesium complex obtained by treating β-bromoethylamine with magnesium ethyl bromide will not react with magnesium.

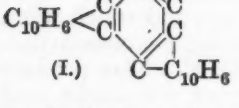
Monochloroacetone is not affected by magnesium but methyl α-chloroethyl ketone undergoes reaction, provided the magnesium is previously amalgamated and some ethyl bromide is used to start the reaction. With *cyclo*hexanone as medium a poor yield of 1-β-*acetylethyl*cyclo*hexan*-1-*ol*, m. p. 123—124°, is obtained. W. A. S.

***o*-Chlorodinitrotoluenes. V. 2-Chloro-3 : 6-dinitrotoluene.** G. T. MORGAN and T. GLOVER (*J. Chem. Soc.*, 1924, **125**, 1597—1601).—The completion of the set of six 2-chlorodinitrotoluenes demanded by theory is realised in the synthesis of 2-chloro-3 : 6-dinitrotoluene. By the action of toluene-*p*-sulphonyl chloride on 6-chloro-*o*-toluidine, 6-*chlorotoluene*-p-*sulphonyl*-o-*toluidide* was obtained, prisms, m. p. 119°, giving when nitrated 6-*chloro*-5-*nitrotoluene*-p-*sulphonyl*-o-*toluidide*, m. p. 157°. Hydrolysis of this gave 6-*chloro*-5-*nitro*-o-*toluidine* (m. p. 162°), which was oxidised by Caro's acid in the cold. 2-*Chloro*-3 : 6-*dinitrotoluene* forms long, colourless needles, m. p. 61·5—63°. 6-*Chloro*-2 : 5-*tolylenediamine*, m. p. 89—90°, was obtained by reducing an alcoholic solution of 6-chloro-5-nitro-*o*-toluidine by means of zinc dust and ammonium chloride. Nitration of 6-chloroaceto-*o*-toluidide gave chiefly 6-chloro-3-nitroaceto-*o*-toluidide, identified by hydrolysis to 6-chloro-3-nitro-*o*-toluidine. W. E. E.

Studies in Chemical Reactivity. II. The Anthracene $\rightleftharpoons$ Dianthracene Reaction, Photochemical and Thermal. H. A. TAYLOR and W. C. MCC. LEWIS.—(See ii, 580.)

Anthracene Derivative. BADISCHE ANILIN- UND SODA-FABRIK and H. HOPFF (D.R.-P. 381180; from *Chem. Zentr.*, 1924, i, 1446).—The following compounds, obtained from the chlorination of anthracene in the presence of pyridine, are mentioned : 9 : 10-*dihydroanthracenedipyridinium chloride*, $C_6H_4<\begin{matrix}CHPyCl\\CHPyCl\end{matrix}>C_6H_4$, crystals, m. p. 180°; *anthranolylpyridinium chloride*, $C_6H_4<\begin{matrix}CH(OH)\\CHPyCl\end{matrix}>C_6H_4$, a brown substance. G. W. R.

Decacyclene. I. Reduction of Decacyclene. K. DZIEWOŃSKI and J. SUSZKO (*Bull. Acad. Polon. Sci. Lett.*, 1923, [*A*], 17—24; from *Chem. Zentr.*, 1924, i, 1377—1378).—By reduction of decacyclene (trinaphthylenebenzene, annexed formula) with hydriodic acid and red phosphorus the following compounds are obtained : *hexahydrodecacyclene*, $C_{36}H_{24}$, a brown, amorphous mass, m. p. 355—365°; *octahydrodecacyclene*, $C_{36}H_{26}$, an amorphous, reddish-brown mass, m. p. 300—310°; *dodecahydrodecacyclene*, $C_{36}H_{30}$, dark red, microcrystalline, m. p. 255°; *hexadecahydrodecacyclene*, $C_{36}H_{34}$, orange-yellow, microcrystalline, m. p.



(I.)

150—160°; *octadecahydrodecacyclene*, $C_{36}H_{36}$, yellow, microcrystalline, m. p. 125—128°; *hexaeikosihydrodecacyclene*, $C_{36}H_{44}$, light yellow oil, b. p. 330—340°/10—12 mm. Structural formulæ, showing hydrogenation by stages of the naphthylene residues, are given for each of the reduction products. G. W. R.

***cyclo*Hexylamines.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 382714; from *Chem. Zentr.*, 1924, i, 1592).—*cyclo*Hexylamines are prepared by heating *cyclo*hexanol with primary or secondary amines or their substitution products and zinc chloride. cyclo*Hexylaniline* is an oil, b. p. 130°/4 mm.; N-cyclo*hexyl*-m-*toluidine*, b. p. 155—160°/13 mm.; N-cyclo*hexyl*-*ethyl*-o-*toluidine*, an oil, b. p. 175°/22 mm. G. W. R.

Reactions of Thiocarbonyl Chloride. I. Reaction with Aromatic Primary Amino Compounds. G. M. DYSON and H. J. GEORGE (*J. Chem. Soc.*, 1924, **125**, 1702—1708).—When an aromatic amine is substituted in the nucleus by a halogen, nitro, or hydroxyl group, the Hofmann method of preparing symmetrically disubstituted thiocarbamides is unsatisfactory. A general method of preparing this type of compound is described, based on the action of thiocarbonyl chloride on aniline, by which phenylthiocarbimide is obtained. The presence of a single halogen atom, hydroxyl, alkoxyl, or carbethoxyl group does not lessen the activity of the amine; the presence of a nitro group increases its activity. Thiocarbimides are obtained when equal weights of thiocarbonyl chloride and amine are used and thiocarbamides when the amine is in excess. The following new compounds are described:—3 : 4-*dimethylphenylthiocarbimide*, pale yellow oil, b. p. 263—264°; 3 : 4-*dimethylphenylthiocarbamide*, by the action of boiling aqueous alcoholic ammonia on the preceding compound, m. p. 141·5—142·5°; s-*di*-3 : 4-*dimethylphenylthiocarbamide*, m. p. 178·5—179°; 2 : 4-*dimethylphenylthiocarbimide*, m. p. 28—29°; 2 : 4-*dimethylphenylthiocarbamide*, m. p. 181·5°; s-*di*-2 : 4-*dimethylphenylthiocarbamide*, m. p. 149—150°; 2 : 5-*dimethylphenylthiocarbimide*, a pale, straw-coloured oil, b. p. 262—263°; 2 : 5-*dimethylphenylthiocarbamide*, m. p. 134·5—135·5°; s-*di*-2 : 5-*dimethylphenylthiocarbamide*, m. p. 148—148·5°; *ψ-cumidylthiocarbimide*, m. p. 22—23°; *ψ-cumidylthiocarbamide*, m. p. 167·5—168°; s-*di*-*ψ*-*cumidylthiocarbamide*, m. p. 145—146·5°; 5-*bromo*-o-*tolylthiocarbimide*, m. p. 48—49°; 5-*bromo*-o-*tolylthiocarbamide*, m. p. 186°; s-*di*-5-*bromo*-o-*tolylthiocarbamide*, m. p. 159°; p-*nitrophenylthiocarbamide*, m. p. 189—190°; 5-*nitro*-o-*tolylthiocarbimide*, m. p. 55—56°; 5-*nitro*-o-*tolylthiocarbamide*, m. p. 188·5°; s-*di*-5-*nitro*-o-*tolylthiocarbamide*, m. p. 130—131°; *nitromesitylthiocarbimide*, pale yellow, hair-like crystals, m. p. 74—75°; s-*di*-(*nitromesityl*)*thiocarbamide*, m. p. 244°; *nitromesitylthiocarbamide*, m. p. 199°; m-*hydroxyphenylthiocarbamide*, m. p. 287° (decomp.); p-*anisylthiocarbamide*, m. p. 210—211°; p-*phenetylthiocarbimide*, m. p. 75—76°; p-*phenetylthiocarbamide*, m. p. 175—176°; s-*di*-p-*phenetylthiocarbamide*, m. p. 171°; o-*carbethoxyphenylthiocarbimide*, yellow oil, b. p. 288—290° (slight

decomp.); o-*carbethoxyphenylthiocarbamide*, m. p. 306—308°; s-*di*-o-*carbethoxyphenylthiocarbamide*, decomp. before melting.

W. E. E.

Halogen-substituted Arylthiocarbimides. F. D. CHATTAWAY, R. K. HARDY, and H. G. WATTS (*J. Chem. Soc.*, 1924, **125**, 1552—1555).—In Hofmann's method of preparing thiocarbimides, the yield of the intermediate carbamide and also that of the final product depend on the nature of the substituents in the aromatic nucleus. Whereas aniline and *o*- and *p*-toluidine react readily with carbon disulphide, their monohalogen derivatives are much less active and their dihalogen derivatives almost inert. When a thiocarbamide, obtained by the addition of phenylthiocarbimide to a halogen-substituted arylamine, is hydrolysed by acid, the more basic unsubstituted residue is removed and a halogen-substituted arylthiocarbimide is produced.

p-*Chlorophenylthiocarbimide*, crystals, m. p. 44·5°, warmed with concentrated aqueous ammonia, gives the corresponding *carbamide*, m. p. 178°. 2 : 4-*Dichlorophenylthiocarbimide*, m. p. 39°, b. p. 208°/17·5 mm. 2 : 4-*Dichlorophenylthiocarbamide*, m. p. 158°. Methyl dichlorophenylthiocarbamate, m. p. 48·5°; corresponding *ethyl* and n-*propyl* esters, m. p. 79° and 72°, respectively. 2 : 4-*Dibromophenylthiocarbimide*, m. p. 59·5°; corresponding *carbamide*, m. p. 170°. *Ethyl* 2 : 4-*dibromophenylthiocarbamate*, m. p. 62°; corresponding n-*propyl* ester, m. p. 68°. n-*Butyl phenylthiocarbamate*, m. p. 55°; n-*butyl* p-*tolylthiocarbamate*, m. p. 65°. p-*Chlorophenyl*-p-*tolylthiocarbamide*, m. p. 173°; p-*chlorophenyl*-o-*tolylthiocarbamide*, m. p. 119·5°; p-*bromophenyl*-p-*tolylthiocarbamide*, m. p. 182°; 2 : 4-*dichlorodiphenylthiocarbamide*, m. p. 157°; 2 : 4-*dibromodiphenylthiocarbamide*, m. p. 165°; 2 : 4-*dichlorophenyl*-p-*tolylthiocarbamide*, m. p. 145°.

W. E. E.

Some Binary Systems composed of Acetic Acid and the Homologues of Aniline. E. A. O'CONNOR (*J. Chem. Soc.*, 1924, **125**, 1422—1427; cf. T., 1921, **119**, 401).—The solid additive compounds formed on mixing certain amines with glacial acetic acid have been isolated and the composition of the liquid phases in equilibrium with these solids determined for various temperatures. *o*-Toluidine forms a *compound*, $C_7H_7\cdot NH_2,C_2H_4O_2$, m. p. 24·8°, deposited over a large range of composition. *m*-Toluidine forms a compound, $C_7H_7\cdot NH_2,2C_2H_4O_2$, existing as a stable α-form, m. p. 10·0°, and a metastable or β-form, m. p. 7·3°. The β-form was metastable to the α-form throughout the range investigated, but no definite conditions for their separation were discovered. The invariant points α- and β-$C_7H_7\cdot NH_2,2C_2H_4O_2$–$C_7H_7\cdot NH_2$–liquid lie at −37·7° and 13% and −39·0° and 16·0% acetic acid, respectively. *p*-Toluidine forms $C_7H_7\cdot NH_2,2C_2H_4O_2$, m. p. 48·0°; mesidine forms $C_9H_{11}\cdot NH_2,C_2H_4O_2$, m. p. 18·9°. Dimethylaniline forms no compound with acetic acid as a solid phase; the heat evolution is extremely small, whilst the complexes of the tertiary amine and acid lack the viscosity at low temperatures characteristic of the primary amines. Combination obviously takes

place in the case of monomethylaniline but no solid phase could be induced to separate. The ratio 1 amine : 1 acid appears to hold where the primary amine possesses a methyl group in the ortho-position; where this is not the case the ratio is 1 amine : 2 acid. The type $2C_6H_5\cdot NH_2,C_2H_4O$ seems to be peculiar to aniline. A. C.

Derivatives of Naphthylaminesulphonic Acids and Aminonaphtholsulphonic Acids. CHEM. FABR. VORM. WEILER-TER MEER and H. SUIDA (D.R.-P. 380578; Austr. Pat. 93324; from *Chem. Zentr.*, 1924, i, 1593—1594).—The patent describes the preparation of colouring matters containing sulphur by the action of sulphur monochloride on salts of naphthylaminesulphonic acids and aminonaphtholsulphonic acids. G. W. R.

Monoiodo Derivatives of *o*-Nitrophenol. I. S. KEIMATSU (*J. Pharm. Soc. Japan*, 1924, No. 507, 319—326).—Hübner's α- and β-iodonitrophenols (*Ber.*, 1874, **7**, 462) are stated to be the 5- and 6-iodo-2-nitrophenols (cf. Beilstein, II, 700). By heating 3-nitro-4-hydroxyphenylarsinic acid (4 g.) with potassium iodide (8 g.) in water (56 c.c.), 5*N*-sulphuric acid (16 c.c.), and alcohol (10 c.c.) during 3 hours, 4-iodo-2-nitrophenol, m. p. 80—81°, is obtained (cf. Roberts, T., 1923, **123**, 2707). When the nitration product, m. p. 214—218°, of *o*-hydroxyphenylarsinic acid (probably a mixture of at least two nitro compounds) is treated with potassium iodide and sulphuric acid as above, a mixture of 6-iodo-2-nitrophenol (obtained by Brenans by the nitration of *o*-iodophenol), and 2-iodo-4-nitrophenol is obtained. It is concluded that Hübner's α- and β-compounds are the 3- and 4-iodo derivatives. K. K.

Derivatives of 2 : 6-Dinitrophenol. E. FROMM and R. EBERT (*J. pr. Chem.*, 1924, [ii], **108**, 75—87).—2 : 6-*Dinitrophenyl benzoate* forms flat needles, m. p. 112°. Bromination of 2 : 6-dinitrophenol in alcohol gives 4-*bromo*-2 : 6-*dinitrophenol*, m. p. 78°; *benzoate*, m. p. 154°; 4-*bromo*-2 : 6-*dinitroanisole* has m. p. 88°. By the action of benzoyl chloride on 2 : 6-diaminophenol hydrochloride is formed 6-*benzamido*-2-*phenylbenzoxazole*, m. p. 222°, and some 2 : 6-*dibenzamidophenol*, m. p. 181°; *benzoate*, m. p. 220°. 2 : 6-*Diacetamidophenol* has m. p. 165°, and its *acetate*, m. p. 224°; *tetra-acetyl*-2 : 6-*diaminophenyl acetate*, m. p. 167°. 6-*Acetamido*-2-*methylbenzoxazole*, obtained by heating 2 : 6-diacetamidophenyl acetate at 230—235°, has m. p. 148°.

2 : 6-*Diaminophenyl* p-*toluenesulphonate* has m. p. 141°; *dibenzoyl* derivative, m. p. 191°; 2 : 6-*di*-p-*toluenesulphonamidophenol*, m. p. 190°.

2 : 6-*Diaminoanisole dihydrochloride* was obtained by reduction of 2 : 6-dinitroanisole; the following derivatives of the base were obtained: *dibenzoyl*, m. p. 157°; *diacetyl*, m. p. 222°; di-p-*toluenesulphonyl*, m. p. 185°. 2 : 6-*Diaminophenetole dihydrochloride* was prepared; 2 : 6-*diacetamidophenetole* has m. p. 240°.

2 : 6-*Diamino*-p-*cresol dihydrochloride* is described; 2 : 6-*diacetamido*-p-*cresol* has m. p. 225—227°; *acetate*, m. p. 228°.

Oxidation of 2 : 6-diacetamidophenol with ferric chloride gives 3 : 5 : 3′ : 5′-*tetra-acetamidodiphenoquinone*, a dark blue, crystalline precipitate, which is reduced by hyposulphite to 3 : 5 : 3′ : 5′-*tetra-acetamido*-4 : 4′-*dihydroxydiphenyl*. With formaldehyde, 2 : 6-diaminophenol forms a *compound*, $C_8H_{10}O_2N_2$,2HCl.

2 : 3 : 6-*Tribenzamidoanisole*, m. p. 225—226°, is obtained by coupling diazobenzene-*p*-sulphonic acid with 2 : 6-diaminoanisole, reducing the azo dye, and benzoylating the resulting triaminoanisole. The last forms with benzil a *quinoxaline* derivative, giving a *hydrochloride*, $C_{21}H_{18}ON_3Cl$, bright red needles. E. H. R.

Chromammines. I. Salts of Nitro and other Dyes. H. J. S. King (*J. Chem. Soc.*, 1924, **125**, 1329—1337).—Dyes containing chelate groups, as those of the quinoneoxime, alizarin, and azosalicylic acid series, readily displace ammonia from the chromammine complex. The chloropentammino- and hexamminochromic salts of the nitro dyes picric acid, aurantia, naphthol-yellow N and S, resemble those obtained from the cobaltammines (T., 1922, **121**, 1723); on boiling they liberate 3 ammonia molecules in about 20 minutes, with precipitation of chromic hydroxide and formation of the ammonium salt of the dye, a reaction which differentiates them from compounds containing chelate groups. It was not found possible to prepare normal hexamminochromic alizarinate, the mono-salt being obtained. Hexamminochromic picramate contains no chelate grouping, possibly indicating that picramic acid has a *p*-quinonoid structure. The alkaline solution obtained from aquopentamminocobaltic chloride and moist silver oxide reacts with naphthol-yellow S as if containing hydroxopentamminocobaltic hydroxide. A. Cousen.

Derivatives of *para*-Substituted Phenylcarbamides. C. F. Boehringer u. Söhne G.m.b.H., L. Ach, and A. Rothmann (D.R.-P. 377816 and 377817; from *Chem. Zentr.*, 1924, i, 964; cf. A., 1923, i, 948). — as-p-*Hydroxyphenylmethylcarbamide*, $N(C_6H_4OH)Me{\cdot}CO{\cdot}NH_2$, forms needles, m. p. 175°; as-p-β-*hydroxyethoxyphenylmethylcarbamide*, $N(C_6H_4{\cdot}O{\cdot}C_2H_4OH)Me{\cdot}CO{\cdot}NH_2$, forms needles, m. p. 140—141°. G. W. R.

Electrochemical Oxidation of the three Tolyl Methyl Ethers. F. Fichter and H. Ris (*Helv. Chim. Acta*, 1924, **7**, 803—813; cf. this vol., i, 282, 629).—Anodic oxidation of *p*-tolyl methyl ether gives methyl alcohol, anisaldehyde, anisic acid, 2-*hydroxy*-2′-*methoxy*-5 : 5′-*dimethyldiphenyl*, an oil, b. p. 205°/12 mm., and 2 : 2′-*dimethoxy*-5 : 5′-*dimethyldiphenyl*, m. p. 71°, b. p. 188°/12 mm. (also prepared by methylating the corresponding diphenol), together with unidentified products of high b. p. The constitution of Fichter and Ackermann's 2 : 2′-dihydroxy-5 : 5′-dimethyldiphenyl (A., 1919, i, 586) was verified by preparing it from *o*-tolidinedisulphonic acid; it yields a *dibenzoyl* derivative, m. p. 136°. Anisaldehyde is converted by anodic oxidation, using a platinum anode, into anisic acid. The oxidation of *p*-tolyl methyl ether in the nucleus, not in the side-chain to anisic acid, is favoured

by high current density, and by using a weak acid and a platinum anode. *m*-Tolyl methyl ether suffers no attack in the side-chain, but is converted into toluquinol (by cathodic reduction of the quinone formed by oxidation), toluquinone, and *4-hydroxy-4′-methoxy-2 : 2′-dimethyldiphenyl*, b. p. 230—235°/12 mm. *o*-Tolyl methyl ether yields methyl alcohol, toluquinol, and a viscous oil, b. p. 190—280°/12 mm., the relative amount of which increases when a higher current density or a platinum anode is used; this appears to be chiefly *4-hydroxy-4′-methoxy-3 : 3′-dimethyldiphenyl*, and gives the corresponding diphenol on demethylation. Toluquinol is oxidised, in cold acetic acid solution containing sulphuric acid, to ditolyldiquinone; its dimethyl ether to 2 : 2′ : 5 : 5′-tetramethoxy-4 : 4′-dimethyldiphenyl, and a quinone (cf. Nietzki and Bernard, A., 1898, i, 529). W. A. S.

o-Hydroxydiphenyl. K. von Auwers and G. Wittig (*J. pr. Chem.*, 1924, [ii], **108**, 99—112).—The reactions of *o*-hydroxydiphenyl are in general similar to those of *o*-cresol. Bromination in acetic acid gives an oily mixture of monobromo derivatives, *3 : 5-dibromo-2-hydroxydiphenyl*, m. p. 56—57°, and *3 : 5 : 4′-tribromo-2-hydroxydiphenyl*, m. p. 151—152° (*methyl ether*, m. p. 98—98·5°, *benzoate*, m. p. 132—133°). By 2*N*-sodium hydroxide the tribromo derivative is converted into a red, amorphous substance.

o-Hydroxydiphenyl reacts slowly with formaldehyde in the cold to form *2-hydroxy-3 : 5-dihydroxymethyldiphenyl*, m. p. 124·5°, which with hydrogen bromide in acetic acid forms *2-hydroxy-3 : 5-dibromomethyldiphenyl*, m. p. 100·5—101°. By the Friedel–Crafts reaction, *o*-diphenyl methyl ether gives *5-acetyl-o-diphenyl methyl ether*, m. p. 91·5—92°; *semicarbazone*, m. p. 209—210°. By heating *o*-hydroxydiphenyl acetate at 130° with aluminium chloride, a mixture of *2-hydroxy-5-acetyldiphenyl* (m. p. 172—173°; *semicarbazone*, m. p. 213°) and *2-hydroxy-3-acetyldiphenyl* (m. p. 60—61°; *semicarbazone*, m. p. 214—215°; *oxime*, m. p. 165—166°) is obtained. *2-Hydroxy-5-ethyldiphenyl* is a pale yellow oil, b. p. 171—172°/18 mm.; *phenylurethane*, m. p. 114—115°.

o-Diphenyl allyl ether, b. p. 166—167°/12·5 mm., $d_4^{20\cdot9}$ 1·0601, $n_\alpha^{20\cdot9}$ 1·58910, changes at 250—300° into *2-hydroxy-3-allyldiphenyl*, b. p. 176—178°/13 mm., $d_4^{18\cdot7}$ 1·0735, $n_\alpha^{18\cdot7}$ 1·59411; *phenylurethane*, m. p. 124·5—125·5°. The allyl derivative changes when heated with methyl-alcoholic potassium hydroxide into *2-hydroxy-3-propenyldiphenyl*, b. p. 185—187°/13 mm., $d_4^{16\cdot3}$ 1·0897, $n_\alpha^{16\cdot3}$ 1·61994; *phenylurethane*, m. p. 166—167·5°; *methyl ether*, b. p. 173—174°/12 mm. Reduction of the propenyl compound with sodium and alcohol gives *2-hydroxy-3-propyldiphenyl*, b. p. 169—172°/13 mm., d_4^{16} 1·0512, n_α^{16} 1·57462; *phenylurethane*, m. p. 126·5—127·5°. Oxidation of the methyl ether of the propenyl compound with permanganate gives *2-methoxydiphenyl-3-carboxylic acid*, m. p. 119—120°.

o-Hydroxydiphenyl propionate, b. p. 168—169°/12 mm., is converted by aluminium chloride into *2-hydroxy-5-propionyldiphenyl*, m. p. 148°. *2-Hydroxy-5-propyldiphenyl* has b. p. 178—179°/12 mm.; *phenylurethane*, m. p. 132—132·5°.

5-Benzeneazo-2-hydroxydiphenyl has m. p. 95—96° and *3 : 5-bis-benzeneazo-2-hydroxydiphenyl*, m. p. 157°. E. H. R.

Univalent Oxygen. III. 9-Chloro-10-phenanthroxyl. S. GOLDSCHMIDT and C. STEIGERWALD (*Annalen*, 1924, **438**, 202—216; cf. A., 1922, i, 1148, 1149).—9-Chloro-10-hydroxyphenanthrene (Schmidt and Lumpp, A., 1909, i, 34) is oxidised in chloroform solution to *9-chloro-10-phenanthryl peroxide*, a colourless substance, m. p. 124—125° (decomp.). In solution, this compound undergoes dissociation into the free radical, *9-chloro-10-phenanthroxyl*, the dissociation being influenced by the presence of traces of hydrogen chloride and therefore proceeding best when pyridine is present; 69% of the substance may then be present as the free radical. When the original oxidation of the chlorophenanthrol is carried out quickly, as by using potassium ferricyanide in aqueous solution, and the product is immediately extracted with chloroform, the free radical is present to the extent of 10% (determined by titration with hydrazobenzene; cf. Goldschmidt and Wolffhardt, this vol., i, 886). The two substances may be separated by fractionally precipitating the chloroform solution with petrol, the peroxide being first thrown down, and the phenanthroxyl separating later as an amorphous blue deposit. 9-Chloro-10-phenanthroxyl resembles its congeners (*loc. cit.*); it unites with bromine to form a yellow compound in which the bromine must be attached to the oxygen atom. W. A. S.

Mechanism of the Action of Potassium Permanganate on Unsaturated Compounds. S. NAMETKIN (*J. pr. Chem.*, 1924, [ii], **108**, 46—51).—By the action of potassium permanganate on unsaturated compounds, glycols are formed, but it has never been decided whether these are produced by hydration of primarily formed oxides. It is shown, by reference to *cyclo*hexanediol and some of its homologues, that this cannot be the case, since hydration of the oxide gives a *cis*-glycol whereas oxidation of the *cyclo*hexene with permanganate gives the *trans*-glycol. It is probable that 2 mols. of permanganate participate in the oxidation, forming at the double bond a complex which by hydration gives a glycol and a manganate, the latter quickly decomposing:

$$\begin{matrix}-CH\cdot O\cdot MnO_2\cdot OK\\ -CH\cdot O\cdot MnO_2\cdot OK\end{matrix} + 2H_2O \rightarrow \begin{matrix}-CH\cdot OH\\ -CH\cdot OH\end{matrix} + 2MnO_4HK.$$

In this way either a *cis*- or *trans*-glycol could be formed, but only the *trans*-isomeride is found. E. H. R.

Molecular Transpositions. Preparation and Dehydration of αα'γ-Triphenyl-ββ-dimethylpropan-α-ol. (MME.) P. RAMART (*Compt. rend.*, 1924, **179**, 276—279).—By the action of magnesium phenyl bromide on benzyldimethylacetophenone, *αα'γ-triphenyl-ββ-dimethylpropan-α-ol*, m. p. 100—101°, distilling without decomposition at 280°/25 mm., is obtained. By the action of thionyl chloride on this, *α-chloro-αα'γ-triphenyl-ββ-dimethylpropane* is obtained. Dehydration of the alcohol by means of a mixture of

acetic anhydride and acetyl chloride yields a mixture of two isomeric *hydrocarbons*, $C_{23}H_{22}$, difficult to separate, m. p. 110° and 89·9° respectively. The latter is converted into the former on treatment with a solution of hydrogen bromide in acetic acid. Dehydration by the action of heat (300—350° at 25 mm.) in the presence of infusorial earth yields *iso*butylbenzene, b. p. 171°, benzophenone, and the hydrocarbon, m. p. 110°. J. W. B.

Application of the Grignard Reaction to some Acetylenic Compounds. II. F. J. Wilson and W. McN. Hyslop (*J. Chem. Soc.*, 1924, **125**, 1556—1558; cf. *ibid.*, 1923, **123**, 2612).—On heating with sulphuric acid, $\alpha\theta$-diphenyl-$\gamma\zeta$-dimethyl-$\Delta^{\alpha\eta}$-octadiinene-$\gamma\zeta$-diol (α modification) is converted into 2 : 5-*diphenylacetylenyl*-2 : 5-*dimethyltetrahydrofuran*, b. p. 206—207°/0·5 mm. Except for some charring, $\alpha\zeta$-diphenyl-$\gamma\delta$-dimethyl-$\Delta^{\alpha\varepsilon}$-hexadiinene-$\gamma\delta$-diol was not affected by this treatment. With sodium hydroxide solution both glycols gave, as the only recognisable product, phenylacetylene. Attempts were made to obtain acetylenic ketols. Diacetyl and magnesium phenylacetylenyl bromide gave *α-phenyl-γ-methyl-*Δ^{α}*-pentinen-γ-ol-δ-one*, b. p. 120°/0·5 mm. (*semicarbazone*, m. p. 171—172°), together with the glycol previously described. When acetonylacetone was subjected to this reaction, only the glycol was obtained. Two tetra-acetylenic glycols have been prepared: *ααββ-tetraphenylacetylenylethylene glycol* (m. p. 147°) from ethyl oxalate and magnesium phenylacetylenyl bromide, and *ααδδ-tetraphenylacetylenyl-αδ-butylene glycol* (m. p. 134—136°) from ethyl succinate and the same Grignard reagent. W. E. E.

Glycol Ethers of certain Aromatic Nitrohydroxy Compounds. O. Matter (D.R.-P. 379881; from *Chem. Zentr.*, 1924, i, 1103—1104).—p-*Nitrophenyl hydroxyethyl ether*,

$$NO_2 \cdot C_6H_4 \cdot O \cdot C_2H_4 \cdot OH,$$

from *p*-chloronitrobenzene and ethylene glycol, has m. p. 96—97°. o-*Nitrophenyl hydroxyethyl ether*, m. p. 37—38°, and 4-*nitronaphthyl hydroxyethyl ether*, m. p. 131—132°, were also prepared. G. W. R.

Thiophenols. VIII. 5-Chloro-2-methylthioltriphenylcarbinols. K. Brand and W. Groebe (*J. pr. Chem.*, 1924, [ii], **108**, 1—18; cf. this vol., i, 852).—By reduction of 4-chloro-2-nitrophenyl methyl sulphide in methyl-alcoholic solution with iron and concentrated hydrochloric acid in presence of copper chloride, 4-*chloro*-2-*aminophenyl methyl sulphide* is obtained, m. p. 29°, b. p. 273—274°, d^{25} 1·2754, n_D^{25} 1·63118; *hydrochloride*, m. p. 198—199°; *nitrate*, unstable, m. p. 148—158°; *sulphate*, m. p. 138—140° (decomp.); *formyl* derivative, m. p. 79—80°; *acetyl* derivative, m. p. 95—96°; *benzoyl* derivative, m. p. 105—106°. Through the diazonium compound (*sulphate*), the amino compound was converted into: 4-*chloro*-2-*bromophenyl methyl sulphide*, m. p. 32—33°; b. p. 140—150°/15 mm.; d^{25} 1·6315; n_D^{16} 1·64223; 2 : 4-*dichlorophenyl methyl sulphide*, b. p. 135—140°/15 mm.; d^{25} 1·3633; n_D^{25} 1·61678; 4-*chloro*-2-*iodophenyl methyl sulphide*, m. p. 26—27°,

b. p. 175—185°/15 mm.; d^{25} 1·881; n_D^{25} 1·6857. When the last was heated with copper bronze at 260—280° it gave 5 : 5′-*dichloro*-2 : 2′-*dimethylthioldiphenyl*, m. p. 160°. 4-*Chloro*-2-*cyanophenyl methyl sulphide*, m. p. 104—105°, is hydrolysed by boiling alcoholic potassium hydroxide to 5-*chloro*-2-*methylthiolbenzoic acid*, m. p. 184—185°; *methyl* ester, m. p. 65—66°. 4-*Chloro*-2-*hydroxyphenyl methyl sulphide* was only obtained in poor yield from the above diazonium sulphate; its *benzoyl* derivative has m. p. 72°.

The magnesium compound of 4-chloro-2-bromophenyl methyl sulphide reacts with benzophenone in presence of a trace of iodine to form 5-*chloro*-2-*methylthioltriphenylcarbinol*, m. p. 111—112°, slightly volatile in steam; the corresponding *chloride* begins to decompose at 114°, m. p. 128°; in concentrated acids the colour is yellowish-green. 5-*Chloro*-2-*methylthioltriphenylmethane* has m. p. 97—98°; with methyl sulphate it forms a *sulphonium methosulphate*, m. p. 186—187°.

Ethyl benzoate reacts with magnesium 5-chloro-2-methylthiolphenyl bromide to form 5 : 5′-*dichloro*-2 : 2′-*dimethylthioltriphenylcarbinol*, m. p. 134—135°; the unstable *chloride* has m. p. 115—126°. 5 : 5′-*Dichloro*-2 : 2′-*dimethylthioltriphenylmethane* has m. p. 120—121°.

From 4-chloro-2-bromophenyl methyl sulphide and methyl 5-chloro-2-methylthiolbenzoate by the Grignard reaction was obtained 5 : 5′ : 5″-*trichloro*-2 : 2′ : 2″-*trimethylthioltriphenylcarbinol*, prisms, m. p. 171—172°, from alcohol and rhombs, m. p. 181—182° from benzene. In a mixture of acetic and sulphuric acids it gives a yellowish-green colour, changing to yellow and then disappearing; the *chloride* reddens at 160°, and has m. p. 170° (decomp.), and the corresponding *triphenylmethane* has m. p. 125—126°. p-*Chlorophenyl methyl sulphide* has b. p. 170°. E. H. R.

Thiophenols. IX. o-Ethylthioltriphenylcarbinols. K. Brand and H. Stein (*J. pr. Chem.*, 1924, [ii], **108**, 19—28).—o-*Nitrophenyl ethyl sulphide*, obtained by reduction of *oo′*-dinitrophenyl disulphide (Brand, A., 1909, i, 855) followed by ethylation of the *o*-nitrophenylmercaptan, has b. p. 172°/10 mm., d^{18} 1·262, n_D^{18} 1·62126. It is reduced by iron and hydrochloric acid (cf. preceding abstract) to o-*aminophenyl ethyl sulphide*, b. p. 144°/15 mm., d^{18} 1·087, n_D^{18} 1·60324. By Sandmeyer's method the last was converted into o-*bromophenyl ethyl sulphide*, b. p. 148°/15 mm., d^{18} 1·4224, n_D^{18} 1·60904; o-*iodophenyl ethyl sulphide*, b. p. 181°/40 mm., d^{18} 1·677, n_D^{18} 1·65687; and o-*cyanophenyl ethyl sulphide*, b. p. 170°/15 mm., d^{18} 1·110, n_D^{18} 1·58570.

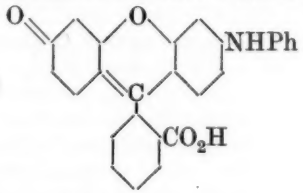
Magnesium *o*-ethylthiolphenyl bromide condenses with benzophenone to give o-*ethylthioltriphenylcarbinol*, m. p. 94°; the corresponding *chloride* has m. p. 117° and o-*ethylthioltriphenylmethane*, m. p. 52°.

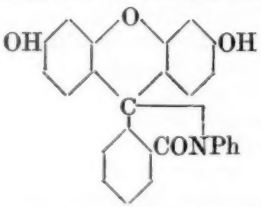
oo′-*Diethylthioltriphenylcarbinol*, m. p. 124°, is obtained by the interaction of the above magnesium compound and ethyl benzoate. The corresponding chloride could not be obtained, but reduction of the carbinol by the method of Kauffmann and Pannwitz (A., 1912, i, 351) gave *oo′*-*diethylthioltriphenylmethane*, m. p. 98°.

Ethyl o-*ethylthiolbenzoate* has m. p. 28°, b. p. 152°/10 mm., d^{30} 1·118, n_D^{30} 1·56309. It reacts with the above magnesium compound to give oo'o''-*triethylthioltriphenylcarbinol*, m. p. 96°; the corresponding *chloride* has m. p. 134°. The colour reactions of the carbinols described are similar to those of the corresponding *o*-methylthiol derivatives (cf. preceding abstract). E. H. R.

Condensation of Fluorescein and Aniline Homologues in Presence of Hydrochloric Acid. T. MAKI (*J. Chem. Ind., Japan*, 1924, **27**, 1—15).—When fluorescein (1 mol.) is heated with aniline, *o*- or *p*-toluidine (7 mols.), and hydrochloric acid (1 mol.) at 210°, a mixture of colourless and coloured anilides or toluidides is produced as follows: *fluoresceinanilide*, $C_{26}H_{17}O_4N$, colourless, m. p. 310—311°, and purple, m. p. 311—312°; *fluorescein*-o-*toluidide*, $C_{27}H_{19}O_4N$, colourless, m. p. 323—324°, and red, m. p. 317—318°; and *fluorescein*-p-*toluidide*, $C_{27}H_{19}O_4N$, colourless, m. p. 322—323° (uncor.), and violet, m. p. 333—334° (uncor.). The colourless anilide gives a *diacetyl* derivative, m. p. 252—253°, and the purple one a *monoacetyl* derivative, m. p. 159—160°. The absorption curve and the position of the point of maximum absorption of the purple anilide indicate a quinonoid structure (I) for this isomeride.

(I.)





(II.)

The wave-lengths of the points of maximum absorption of the purple anilide and its homologues are as follows: purple anilide, 5550, red *o*-toluidide, 5330, violet *p*-toluidide, 5570. It is considered that the lactone form of fluorescein is converted into the purple anilide and that the colourless anilide is derived from the quinonoid form of fluorescein. Formula II is suggested for the colourless anilide. K. K.

Preparation of Nitriles from Acid Amides. FARBWERKE VORM. MEISTER, LUCIUS, UND BRÜNING, E. SCHIRM, and F. HENLE (D.R.-P. 380323; from *Chem. Zentr.*, 1924, i, 1272).—Nitriles are prepared by the action of sulphochlorides of the benzene or naphthalene series on acid amides in the presence of alkali halides or of tertiary bases. Acetonitrile and benzonitrile are prepared from the corresponding amides. G. W. R.

o-Aminobenzenecarboxylic Acids. KALLE U. CO., AKT.-GES. and M. SCHMIDT (D.R.-P. 375616; from *Chem. Zentr.*, 1924, i, 966).—*o*-Aminocarboxylic acids are prepared by oxidation of isatin and its derivatives, particularly with hydrogen peroxide in alkaline solution. 5-*Bromo*-2-*amino*-m-*toluic acid* has m. p. 229°.

G. W. R.

N-Substituted Derivatives of Aminobenzoic Acid. C. F. BOEHRINGER U. SOEHNE G.M.B.H. (Austr. Pat. 94307; Swiss Pat. 101513; from *Chem. Zentr.*, 1924, i, 1595).—The following new compounds are mentioned: N-2-*phenylquinoline*-4-*carboxylanthranilic acid*, $C_9H_5N(Ph)\cdot CO\cdot NH\cdot C_6H_4\cdot CO_2H$, m. p. 226—227°; 2-(2′-*carboxyphenylamino*)*quinoline*-4-*carboxylic acid*, $CO_2H\cdot C_9H_5N\cdot NH\cdot C_6H_4\cdot CO_2H$, m. p. 301° (decomp.), *dimethyl* ester, m. p. 164°; N-2-*phenyl*-6-*methylquinoline*-4-*carboxylanthranilic acid*, m. p. 212°, *methyl* ester, m. p. 155—156°; condensation *compound* from 2-phenylquinoline-4-carboxylic chloride and 4-chloroanthranilic acid; 2-(2′-*carboxy*-4′-*hydroxyphenylamino*)*quinoline*-4-*carboxylic acid*, m. p. about 280°; condensation *compound* from 2-phenylquinoline-4-carboxylic chloride and *p*-aminobenzoic acid, m. p. 282°; the corresponding *compound* with *m*-aminobenzoic acid, m. p. 287°; 2-(3′-*carboxyphenylamino*)*quinoline*-4-*carboxylic acid* and 2-(4′-*carboxyphenylamino*)*quinoline*-4-*carboxylic acid*, m. p. above 305°. G. W. R.

Formula of Anthranil. E. BAMBERGER (*Helv. Chim. Acta*, 1924, **7**, 814—815).—Objections are raised (cf. A., 1903, i, 432, etc.) to the "nitrone" formula suggested by Staudinger and Miescher (A., 1919, i, 584). W. A. S.

Catalytic Racemisation of the Diastereoisomeric *l*-Menthyl Phenylbromoacetates. A. MCKENZIE and I. A. SMITH (*J. Chem. Soc.*, 1924, **125**, 1582—1593; cf. *ibid.*, 1923, **123**, 1962).—The production of *l*-menthyl αα-phenylbromoacetate in the esterification of *l*-phenylbromoacetic acid by *l*-menthol in the presence of hydrogen chloride shows that *l*-phenylbromoacetic acid is catalytically racemised by hydrogen chloride; *l*-menthol + *l*-phenylbromoacetic acid ⟶ *l*-menthyl *l*-phenylbromoacetate + *l*-menthyl *d*-phenylbromoacetate. Crystallisation of the mixture gives the *d*-isomeride. When heated with alcoholic hydrogen chloride, the *d*-ester racemises to a mixture of *d*- and *l*-esters, in which the *l*-ester slightly predominates. When esterified in the presence of sulphuric acid, the *d*-acid gives *d*-ester. One or two drops of alcoholic alkali produce catalytic racemisation, the rate of which is greater in the case of *d*-ester than in the case of *l*-ester. Moreover, notably in the case of *l*-menthyl *d*-phenylchloroacetate, the proportions of the two optical isomerides at the end of the racemisation were not equal. The cause of this can be ascribed to the directive influence of the asymmetrical *l*-menthyl group. The following compounds are described:—l-*Menthyl* d-*phenylbromoacetate*, m. p. 78—79°, $[\alpha]_D^{18}$ +9·4°, $[\alpha]_{5461}^{18}$ +13·2° in ethyl alcohol. l-*Menthyl* l-*phenylbromoacetate*, m. p. 40—41°, $[\alpha]_D^{15}$ −146·1°, $[\alpha]_{5461}^{15}$ −172·8° in ethyl alcohol; $[\alpha]_D^{17}$ −139·8°, $[\alpha]_{5461}^{17}$ −166·9° in benzene. *l*-Phenylbromoacetic acid has $[\alpha]_D^{14}$ −147·7° in benzene. W. E. E.

Constitution of Curcumone from Curcuma [Turmeric] Oil. H. RUPE and F. WIEDERKEHR (*Helv. Chim. Acta*, 1924, **7**, 654—669; cf. A., 1911, i, 293).—When curcuma oil is treated with ozone an acid is obtained which is now shown to be identical with (not, as

was at first supposed, different from) curcumic acid, $C_{11}H_{14}O_2$. The latter has m. p. 42—43°, b. p. 163—164°/10 mm., $[\alpha]_D^{20}$ +46·53° or +47·58° according to the method of preparation. Its *ethyl* ester has b. p. 133—134°/10 mm.; the *calcium* and *silver* salts of the acid are described.

p-Tolyl methyl ketone reacts with ethyl bromoacetate and zinc to give a mixture of esters (b. p. 150—153°/9 mm.) which, when hydrolysed by alcoholic potassium hydroxide yields chiefly p-*tolyl*-Δ^{α}-*butenoic acid*, needles, m. p. 135°, together with a little β-hydroxy-β-*p*-tolylbutyric acid. *Ethyl* p-*tolyl*-Δ^{α}-*butenoate* has b. p. 145—156°/10 mm. When *p*-tolyl-Δ^{α}-butenoic acid is reduced with hydrogen and a nickel catalyst, β-p-*tolylbutyric acid*, $C_{11}H_{14}O_2$, m. p. 91°, b. p. 165°/10 mm., is formed; its *chloride* has b. p. 125°/9 mm.; the *p-toluidide*, m. p. 112—113°, the *ethyl* ester, b. p. 133—135°/10 mm., and the *calcium* salt are described. This synthetic acid has the same b. p. as curcumic acid; the esters also resemble one another. Only in m. p. and optical activity do the two acids differ. They give similar products when oxidised with cold dilute potassium permanganate solution: curcumic acid yields *p*-tolyl methyl ketone and an optically active dibasic *acid*, $C_{11}H_{12}O_4$, m. p. 227—229°, $[\alpha]_D^{20}$ +35·34°, whilst the synthetic acid yields *p*-tolyl methyl ketone and an optically inactive acid of the same composition and m. p. (226°), presumably β-p-*carboxyphenylbutyric acid*. A mixture of the two acids has m. p. 225—227°. Curcumic acid is thus proved to be *d*-β-*p*-tolylbutyric acid.

β-*p*-Tolylbutyryl chloride and zinc methyl yield β-p-*tolylpropyl methyl ketone*, $Me{\cdot}C_6H_4{\cdot}CHMe{\cdot}CH_2{\cdot}CO{\cdot}Me$, b. p. 130·5°/11 mm., d_4^{20} 0·9598; *oxime*, b. p. 165—166°/13 mm., *semicarbazone*, m. p. 145—146°, *azine*, b. p. 245—246°/11 mm., *benzylidene* derivative, m. p. 88°. Curcumone has b. p. 130°/11 mm., d_4^{20} 0·9618; it yields an optically active *oxime*, b. p. 165—166°/13 mm., a *semicarbazone*, m. p. 121°, an optically active *azine*, b. p. 245—246°/11 mm., and a *benzylidene* derivative, m. p. 106°. Curcumone is therefore *d*-β-*p*-tolylpropyl methyl ketone.

Before the true nature of the acid obtained by ozonising curcuma oil was discovered attempts were made to reproduce it synthetically. When *p*-tolylacetonitrile is treated in ethereal solution with sodamide followed by methyl iodide, it affords the nitrile of *p*-methylhydratropic acid (b. p. 123°/12·5 mm.; cf. Errera, A., 1892, 605) which, on hydrolysis, yields p-*methylhydratropic acid*, m. p. 34°, b. p. 161—161·5°/12·5 mm., *chloride*, b. p. 122—123°/13·5 mm., *amide*, m. p. 195°, p-*toluidide*, m. p. 102—103°. The latter is accompanied by a little p-*tolylaceto*-p-*toluidide*, m. p. 163°, and after purification serves as a convenient source of pure samples of the parent acid. *Ethyl* p-*methylhydratropate* has b. p. 123·5°/11 mm. Similarly, by using ethyl iodide in the first reaction, α-p-*tolylbutyric acid*, m. p. 67—68°, b. p. 160—161°/11 mm., is prepared, *via* its *nitrile*, b. p. 135°/14 mm. The *chloride* has b. p. 118—120°/12 mm., the *amide* m. p. 105°, the p-*toluidide* m. p. 118°; the *methyl* ester (b. p. 123°/10 mm.), the *ethyl* ester (b. p. 130°/11·5 mm.), and the *magnesium* salt also are described. W. A. S.

Acid Constituents of the Gum of the Aleppo Pine. I. α- and β-Alepic Acids. G. DUPONT (*Bull. Soc. chim.*, 1924, [iv], **35**, 879—889).—The gum is separated by compression into solid and liquid constituents. By dissolving the dry solid in the minimum amount of cold ethyl alcohol and fractionally precipitating with water, samples are obtained which on rapid recrystallisation from cold acetone give a mixture of crystals of two isomeric acids, $C_{20}H_{30}O_2$, termed α- and β-alepic acids. The crystalline forms of the two acids are distinct. *α-Alepic acid* forms orthorhombic prisms, m. p. 148°, $[\alpha]_D$ −66°; *β-alepic acid* forms clinorhombic prisms, m. p. 157—159°, $[\alpha]_D$ −66·8°. Both acids are easily isomerised to α-abietic acid, expecially in alcoholic solution in presence of a trace of hydrochloric acid. The rotatory power of the α-acid falls to $[\alpha]_D$ −12·4° and then rises to $[\alpha]_D$ −84·4°, whereas the minimum value shown by the β-acid under these conditions is $[\alpha]_D$ −55·0°, rising finally to $[\alpha]_D$ −86·0°, the value for α-abietic acid being −104°, and m. p. 173°.

The author considers that in the change from α-alepic acid to α-abietic acid, an intermediate alepabietic acid is first formed, whereas the β-acid changes directly into α-abietic acid. α-Abietic acid was isolated from the last of the fractional precipitations by water from the alcoholic solution of the pressed gum, which contains about 75% of α- and 25% of β-alepic acid. A. E. C.

Acids contained in the Gum of the Aleppo Pine. II. G. DUPONT and L. DESALBRES (*Bull. Soc. chim.*, 1924, [iv], **35**, 890—892).—The authors have isolated alepabietic acid (cf. preceding abstract) and shown that β-alepic acid is merely an isomorphous mixture of alepabietic acid and abietic acid. Aleppo pine gum contains α-alepic acid and a certain amount of alepabietic acid and abietic acid. The isomorphism of the two latter acids is proved by crystallographic measurements. A. E. C.

The Phenylalanine Series. V. Hydrogenation of Tyrosine. E. WASER and E. BRAUCHLI (*Helv. Chim. Acta*, 1924, **7**, 740—758; cf. A., 1923, i, 337, 338).—The physical constants and other properties of hexahydrotyrosine already recorded (*loc. cit.*) are incorrect. When tyrosine is catalytically reduced with platinum black, hexahydrophenylalanine is always produced to some extent. Thus, when the hydrogenation is carried out in acid solution, about 75% of the material suffers this change; in neutral suspension, 40—44%; in alkaline suspension very little, *viz.*, only about 16%. Only a little alkali is needed (0·04 equivalent of potassium hydroxide); if one equivalent be present, practically no action takes place. Phenol behaves in a similar way (cf. Willstätter and Hatt, A., 1912, i, 845). Pure hexahydrotyrosine was separated as the ethyl ester. The regenerated l-*hexahydrotyrosine* has m. p. (in a sealed tube, quickly heated) 285° (decomp.), $[\alpha]_D^{20}$ +14·65° (in acid solution); its *hydrochloride* has m. p. 238° (decomp.) The *ethyl* ester (which cannot be obtained by hydrogenating tyrosine ester, only hexahydrophenylalanine ester being formed) has m. p. 99—100°, b. p. 184·5°/11 mm., $[\alpha]_D^{20}$ +15·19°; *hydrochloride*, m. p. 261° (decomp.). N-p-*Nitro-*

benzoylhexahydrotyrosine has m. p. 225—226°. 3 : 6-*Di*-p-*hydroxyhexahydrobenzyl*-2 : 5-*diketopiperazine*, which remains behind when the ester is distilled, has m. p. 332° (decomp.). Hexahydrotyrosine yields a *phenylcarbimido* compound, m. p. 112° ($1H_2O$) or 141°, decomp. 145° (anhydrous); when a solution containing this compound and sulphuric acid is evaporated, the *phenylhydantoin* derivative, m. p. 206·5°, is obtained. *l*-Hexahydrophenylalanine, separated from the above, has m. p. 324° (decomp.) or 282° (decomp.), and $[\alpha]_D^{20}$+13·30°; its hydrochloride has m. p. 246°; the chloroplatinate, benzoyl, and other derivatives have already been described (*loc. cit.*) as hexahydrotyrosine chloroplatinate, etc. The *ethyl* ester, obtained as described, either directly or by hydrogenating tyrosine ethyl ester, has b. p. 149—150°/11 mm., $[\alpha]_D^{20}$ +11·45°, and forms a *hydrochloride*, m. p. 195—196°. When *d*-phenylalanine is hydrogenated the *l*-isomeride ($[\alpha]_D^{20}$+13·32°) is produced, and the racemic form, also with m. p. 246°, is obtained from *dl*-phenylalanine. When tyramine and *p*-methoxyphenylalanine are catalytically reduced the chief product, in both cases, is *cyclo*hexylethylamine.

Addendum. A New Characteristic Colour Reaction for α-Amino-acids.—When 1 mg. or more of an α-amino-acid (23 compounds gave positive results) is dissolved in 3—4 c.c. of 10% sodium carbonate solution, the solution heated and a few crystals of *p*-nitrobenzoyl chloride are added, a transient but very intense dark red or violet coloration is produced. The reaction is specific for nitrobenzoyl chloride and, as stated, for α-amino-acids, with the exception of glycine and cystine. W. A. S.

α-Naphthol-4-carboxyarylamides. Society of Chemical Industry in Basle (Swiss Pats. 100363, 100364, 100365; from *Chem. Zentr.*, 1924, i, 2011; cf. this vol., i, 173).—The following compounds are described: α-*naphthol*-4-*carboxy*-o-*toluidide*, m. p. 238°; α-*naphthol*-4-*carboxy*-p-*toluidide*, m. p. 215°; α-*naphthol*-4-*carboxy*-N-*methylanilide*, m. p. 232°. G. W. R.

Ketobutyric Acids. Farbwerke vorm. Meister, Lucius, u. Brüning and F. Mayer (D.R.-P. 376635; from *Chem. Zentr.*, 1924, i, 966—967).—Ketobutyric acids are obtained by the condensation of succinic anhydride with hydrocarbons and their derivatives. Condensation *compounds* (ketobutyric acids) of succinic anhydride with the following compounds are mentioned: with α-naphthyl methyl ether, m. p. 174°; with fluorene, m. p. 109°; with anthracene, m. p. 160°; with diphenylene oxide, m. p. 185°; with acenaphthene, m. p. about 202—203°; with dihydroanthracene, m. p. 156·5—157·5°. G. W. R.

Aromatic Dimethylamines. Kalle und Co., Akt.-Ges. (D.R.-P. 375463; from *Chem. Zentr.*, 1924, i, 966).—Phenyliminodiacetic acid or its derivatives are treated with ferrous sulphate, ferric sulphate, or ferric oxide in acid solution. The following compounds are mentioned: o-*tolyliminodiacetic acid*; *dimethyl*-

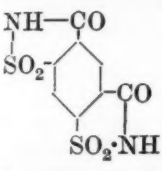
o-*toluidine*; p-*ethoxyphenyliminodiacetic acid*, m. p. 120°; *dimethyl*-p-*phenetidine*. G. W. R.

Melting Point of Acetylsalicylic Acid. M. E. PUTNAM (*Ind. Eng. Chem.*, 1924, **16**, 778).—The melting point of pure acetylsalicylic acid, considered as the temperature of formation of the first liquid globule in a sample contained in a melting-point tube inserted in a bath at 130°, the temperature of which is rising at exactly 3° per minute, is 133·5°. F. G. W.

***s*-*N*-Aminophthalimide.** M. A. MIHĂILESCU and L. FLORESCU (*Bull. Acad. Sci. Roumaine*, 1923, **8**, 303—320; cf. A., 1912, i, 311).—The action of a concentrated aqueous solution of hydrazine sulphate and sodium acetate on a boiling solution of phthalic anhydride in glacial acetic acid yields a product isomeric with those previously obtained by Rottemburg (A., 1894, i, 285) and Försterling (A., 1895, i, 354) to which the constitution $C_6H_4<^{CO}_{CO}>N\cdot NH_2$ is attributed. s-N-*Aminophthalimide* melts above 340° without subliming. It is sparingly soluble in hot water, hydrolysing slightly to *N*-aminophthalamic acid. The potassium salt, $C_8H_7O_5N_2K$, is identical with that obtained by Försterling from phthalylhydrazide, $C_6H_4<^{CO\cdot NH}_{CO\cdot NH}$, to which accordingly the structure $C_6H_4(CO_2K)CO\cdot NH\cdot NH_2$, is now assigned. Only monometallic salts could be obtained and these are precipitated from solution by alcohol, but not by carbon dioxide. They are converted by acids into the original *N*-aminophthalimide. *Diacetyl*-N-*aminophthalimide*, m. p. 132°, by crystallisation from alcohol or boiling water is converted into the *monoacetyl* derivative, $C_{10}H_8O_3N_2$, m. p. 170°. The *monobenzoyl* derivative, m. p. 220—222°, sublimes at 200°. No condensation product could be obtained with acetone or with aliphatic aldehydes or with benzaldehyde. *N*-Aminophthalimide and cinnamaldehyde yield *cinnamylidene*-N-*aminophthalimide*, $C_6H_4<^{CO}_{CO}>N\cdot N{:}CH\cdot CH{:}CHPh$, m. p. 224°. p-*Methoxybenzylidene*-N-*aminophthalimide* has m. p. 188—190°. R. B.

Disaccharins. A. F. HOLLEMAN and H. J. CHOUFOER (*Proc. K. Akad. Wetensch., Amsterdam*, 1924, **27**, 353—360).—The compound of m. p. 129° described by Wischin (A., 1891, 73) as 1 : 3-xylene-2 : 4-disulphochloride on account of its conversion, by heating with phosphorus pentachloride, into 2 : 4-dichloro-*m*-xylene, has been shown to be the dichloride of the 4 : 6-disulphonic acid by synthesis from 6-nitro-*m*-xylene by the following steps: $C_6H_3Me_2NO_2(1:3:6) \longrightarrow C_6H_2Me_2(SO_3H)\cdot NO_2(1:3:4:6) \longrightarrow C_6H_2Me_2(SO_3H)\cdot NH_2 \longrightarrow C_6H_2Me_2(SO_3H)\cdot SH \longrightarrow C_6H_2Me_2(SO_3H)_2(1:3:4:6)$; cf. Pfannenstill (Dissertation, Lund, 1894), and Pollak and Lustig (this vol., i, 30). Some change of orientation must therefore have occurred in Wischin's experiment. This disulphochloride is also the chief product of the action of chlorosulphonic acid on *m*-xylene. It yields a *disulphonamide*, m. p.

249°, which is oxidised by permanganate to the *disaccharin*, iso-*phthalicdisulphinide* (annexed formula), m. p. 268—270°, of acid and bitter taste.



The other possible disaccharin derived from *m*-xylene has not yet been prepared, but the oily disulphochloride of a disulphonic acid isolated as a by-product in the sulphonation of *m*-xylene-2-sulphonic acid (Pfannenstill, *loc. cit.*) probably has the required structure, $C_6H_2Me_2(SO_3H)_2(1:3:2:4)$. It yields a *disulphonamide*, m. p. 220°.

Direct sulphonation of *p*-xylene yields the 2 : 6-disulphonic acid, and its disulphonamide does not yield a di-imide on oxidation. *p*-Xylene-2 : 5-disulphonic acid was synthesised from the *p*-xylidine-sulphonic acid, $C_6H_2Me_2(NH_2)(SO_3H)(1:4:2:5)$, by replacing the amino group by a sulphonic group. The *disulphochloride*, m. p. 162°, is identical with a by-product observed by Pfannenstill in the action of chlorosulphonic acid on *p*-xylene. It yields a *disulphonamide*, m. p. 310°, oxidised by permanganate to *terephthalic*-2 : 5-*disulphinide*, m. p. 320°, of bitter taste.

A liquid o-*xylenedisulphochloride* was prepared through the stages: $C_6H_3Me_2(NH_2)(1:2:6) \longrightarrow C_6H_2Me_2(SO_3H)\cdot NH_2(1:2:3:6) \longrightarrow C_6H_2Me_2(SO_3H)\cdot SH \longrightarrow C_6H_2Me_2(SO_3H)_2$, but the orientation of these compounds has not been finally established. The chloride yields a *disulphonamide*, m. p. 251°, converted by permanganate into a *phthalicdisulphinide*, m. p. 275—280°, of bitter taste.

G. M. B.

Ester of Cholic Acid. Gehe u. Co., Akt.-Ges., and H. Reume (D.R.-P. 375370 and 381350; from *Chem. Zentr.*, 1924, i, 969).—*Benzyl cholate* is a greyish-white powder, softening at about 69°.

G. W. R.

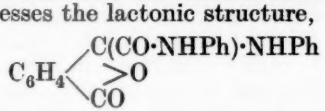
Additive Compounds of Cholic Acid. C. H. Boehringer Sohn, Chemische Fabrik (D.R.-P. 376470; from *Chem. Zentr.*, 1924, i, 968—969).—The preparation of *additive* compounds of cholic acid with the following aliphatic esters is described: ethyl lactate; amyl acetate; ethyl carbamate; ethyl chloromalonate; bornyl valerate; ethyl butyrate. G. W. R.

Derivatives of *p*-Aminophenol. Kalle u. Co., Akt.-Ges., and E. Spröngerts (D.R.-P. 383190; from *Chem. Zentr.*, 1924, i, 1592).—The following new compounds are mentioned: p-*ethoxyphenyliminodiacetic acid*, from *p*-phenetidine and chloroacetic acid, m. p. 118° (decomp.); p-*hydroxyphenyliminodiacetic acid*, from *p*-aminophenol and chloroacetic acid, m. p. 165° (decomp.).

G. W. R.

Constitution of Phthalonic Acid. Its Compounds with Aniline. A. Cornillot (*Compt. rend.*, 1924, **179**, 274—276; cf. this vol., i, 288, 515).—Evidence for the structure of phthalon-2-anilic acid and phthalondianilide, prepared by Kuroda and Perkin (T., 1923, **123**, 2094), is deduced. The dianilide is stable

towards acids and dissolves in concentrated solutions of alkalis and therefore possesses the lactonic structure,



It does not react with semicarbazide, but reacts readily as a secondary amine to yield a *phenylurethane*, m. p. 203·5°. The structure is confirmed by its synthesis from aniline and the anilide of α-chlorophthalonic acid. The anilic acid reacts with excess of aniline in benzene solution to yield only the dianilide (the aniline α-anilino-α-hydroxyhomophthalanilate described by Kuroda and Perkin, *loc. cit.*, not being obtained) and therefore behaves as if it possessed the lactonic structure. In alcohol solution, however, a small quantity of an amorphous acid which has the same empirical formula as the dianilide and yields colloidal solutions is obtained. This is the *phenylimine* of phthalon-2-anilic acid,

$$[CO_2H\cdot C_6H_4\cdot C(:NPh)\cdot CONPh]_x,$$

and can only be derived from the ketonic form of the anilic acid. The action of thionyl chloride on the anilic acid yields the anilide of α-chlorophthalonic acid as the main product but in addition a small quantity of the N-*phenylphthalonimide*, m. p. 217°, is produced by dehydration of the ketonic form. The anilic acid thus reacts mainly in its lactonic form but contains a small quantity of the ketonic modification. J. W. B.

α- and β-Disalicylides. R. Anschütz and K. Riepenkröger (*Annalen*, 1924, **439**, 1—8; cf. A., 1920, i, 48).—Salicyloyl chloride heated at 20 mm. begins to lose hydrogen chloride at 110°, decomposition being complete at 180°, and the chloroform solution of the product deposits polysalicylide, whilst the mother-liquor contains the tetrasalicylide. *o*-Diplosal chloride (*o*-salicyloylsalicyloyl chloride) similarly yields a mixture of the poly- and tetra-salicylides. The α-disalicylide is also obtained when diethylaniline is added to an ice-cold solution of salicyloyl chloride in benzene. The product obtained by the action of α-disalicylide on aniline or *p*-toluidine is shown to be the *N*-salicyloyl derivative of the base by the conversion of *o*-diplosalanilide into O-*acetyl*-o-*diplosalanilide*, m. p. 140—141°, which is also obtained by the action of aniline in dry ether on O-*acetyl*-o-*diplosal chloride*, m. p. 104—105°. o-*Diplosalamide* on heating is converted into disalicyloylimide. By excess of ammonia the amide is converted into the ammonium salt of the imide, and by acetyl chloride, in the presence of pyridine, into O-*acetyl*-o-*diplosalamide*, $OAc\cdot C_6H_4\cdot CO_2\cdot C_6H_4\cdot CONH_2$, m. p. 158—159°. *Diacetyldisalicyloylimide*, $(OAc\cdot C_6H_4\cdot CO)_2NH$, has m. p. 114—116°. The β-disalicylide treated with an equimolecular quantity of ammonia in chloroform solution, slowly forms only the yellow ammonium salt of the disalicoylimide, and reacts with aniline only at 155—165°, forming salicoylanilide. J. W. B.

α-Dicresotides. R. Anschütz (*Annalen*, 1924, **439**, 8—19).—By the distillation of the three *O*-acetylcresotic acids under reduced

pressure, *o*-, *m*-, and *p*-α-dicresotides corresponding with the disalicylides (cf. preceding abstract) are obtained. No corresponding β-dicresotides were isolated. They are also obtained in good yields by the distillation of the phenyl ester of the respective cresotic acid under 100 mm. Subsequent distillation under 12 mm. yields the dicresotide. By the action of diethylaniline in benzene solution on the *o*-, *m*-, and *p*-cresotoylcresotoyl chlorides (dimethyldiplosal chlorides), hydrogen chloride is split off and the corresponding α-dicresotide produced. Distillation of the α-dicresotide under ordinary pressure yields the corresponding dimethylxanthone. The dicresotides give a series of derivatives corresponding with those of the disalicylides.

[With F. Post and E. Corty.]—Fractional crystallisation, from chloroform, of the product of distillation of acetyl-*o*-cresotic acid yields also the tetra-*o*-cresotide (α-homosalicylide, A., 1893, i, 166) and by heating under 18 mm. this is practically completely converted into α-dicresotide. *Methyl* o-*cresotoyl*-o-*cresotate* has m. p. 56°. *Di*-o-*cresotoylimide*, $[OH{\cdot}C_6H_3Me{\cdot}CO]_2NH$, m. p. 170°, with excess of ammonia yields the *ammonium* salt, from which the corresponding *silver*, *mercury*, *copper*, *calcium*, *strontium*, and *barium* salts are obtained. It forms an *anilide*, and a p-*toluidide*, m. p. 184°.

[With K. Riemar and E. Corty.]—α-Di-*m*-cresotide is identical with that obtained by Einhorn and Mettler (A., 1903, i, 30). *Phenyl acetyl*-m-*cresotate* has m. p. 71—72°; m-*cresotoylamide*, m. p. 182·5°; m-*cresotoyl*-m-*cresotic acid*, m. p. 162°, *chloride*, m. p. 122°, *methyl* ester, m. p. 115°, *amide*, which on heating yields the *imide*, m. p. 211—212°, forming an *ammonium* salt from which the corresponding *silver*, *mercury*, *copper*, *calcium*, *strontium*, and *barium* salts are obtained; *anilide*, m. p. 189°, p-*toluidide*, m. p. 202°.

[With R. Inderhees and A. Lüssem.]—α-*Di*-p-*cresotide* has m. p. 197—199°. The *tetra*-p-*cresotide* obtained, by extraction with hot chloroform, from the product of the distillation of acetic acid, acetic anhydride, and *p*-cresotic acid is converted practically completely into the α-di-*p*-cresotide by distillation under 12 mm.; *p*-cresotoyl-*p*-cresotic acid, m. p. 128—129°; *chloride*, m. p. 93—95°; *methyl* ester, m. p. 104—105°; *ethyl* ester, m. p. 97—98°; *acetyl* derivative, m. p. 133—134°; *anilide*, m. p. 159—160°, p-*toluidide*, m. p. 176—177°. The amide on heating yields the *imide*, m. p. 173—174°, of which *ammonium*, *silver*, *mercury*, *copper*, *calcium*, *strontium*, and *barium* salts are described. *Diacetyldi*-p-*cresotoylimide* has m. p. 140—141°. J. W. B.

Menthyl αγ-Diacetyl-β-methylglutarate. H. Rupe and F. Becherer (*Helv. Chim. Acta*, 1924, **7**, 670—681).—The following results were obtained in an abortive effort to prepare an alcohol possessing high optical activity. Menthyl acetoacetate (A., 1913, i, 884) and acetaldehyde undergo the Knoevenagel condensation and yield two isomeric forms of *menthyl αγ-diacetyl-β-methylglutarate*. The chief product has m. p. 200° and $[\alpha]_D^{20}$ −49·01°, and affords a *semicarbazone*, m. p. 196—197°; the subsidiary product, not

isolated in every case, has m. p. 152° and $[\alpha]_D^{20}$ −26·48°, its *semicarbazone* melting at 165—166°. The second form is converted into the first by recrystallisation from benzene, the product having, however, $[\alpha]_D^{20}$ −68·01°. When ethyl αγ-diacetyl-β-methylglutarate is heated with one molecular proportion of menthol at 150—160°, *menthyl ethyl αγ-diacetyl-β-methylglutarate*, m. p. 154—155°, $[\alpha]_D^{20}$ −28·99°, is obtained (*semicarbazone*, m. p. 169—170°); this, heated with more menthol, affords the second form, m. p. 152—153°, of the ester described above. The ester of m. p. 200° is converted by treatment in ethereal solution with a little hydrogen chloride into *menthyl 5-keto-1 : 3-dimethyl-*Δ^6*-cyclohexene-2 : 4-dicarboxylate*, m. p. 185—186°, $[\alpha]_D^{20}$ −27·90°, *semicarbazone*, m. p. 179—180°, whilst the ester of m. p. 152°, similarly treated, yields a stereoisomeric form of this cyclic compound, m. p. 137—138°, $[\alpha]_D^{20}$ −56·27°, *semicarbazone*, m. p. 104—105°. The isomerism of the above compounds is discussed, it being pointed out that all three carbon atoms in the glutaric acid "spinal column" are asymmetric. Reduction of the menthyl ethyl αγ-diacetyl-β-methylglutarate by Bouveault and Blanc's method failed to give a primary alcohol and hydrolysis of the dimenthyl ester did not take place normally. W. A. S.

Attempts to Synthesise Benzophenone-2 : 3′ : 4′-tricarboxylic Acid. H. DE DIESBACH and P. BULLIARD (*Helv. Chim. Acta*, 1924, **7**, 618—627).—Benzophenone-2 : 3′ : 4′-tricarboxylic acid, Limpricht's "phthaloylphthalic acid," can easily be produced from *o*-xylene, but pure supplies of the latter are not readily obtainable. The preparation of the compound by other methods has therefore been investigated. 3′-Amino-4′-methylbenzophenone-2-carboxylic acid (Limpricht, A., 1898, i, 322) is converted by the Sandmeyer reaction into *3′-cyano-4′-methylbenzophenone-2-carboxylic acid*, m. p. 194°, of which the *methyl* ester, m. p. 87·5°, and the *copper* salt are described. This nitrile is not hydrolysed by sulphuric acid without condensation to anthraquinone derivatives also taking place, but boiling 30% potassium hydroxide converts it into the expected *4′-methylbenzophenone-2 : 3′-dicarboxylic acid*, m. p. 216°; *dimethyl* ester, m. p. 94°. Treatment of the nitrile with nitric acid, *d* 1·15 at 200° for 8 hours, brings about simultaneous oxidation and hydrolysis, "phthaloylphthalic acid" being obtained. The product has m. p. 199·5°, higher than any previously recorded.

The conversion of 2 : 3′-dichloro- or -dibromo-4′-methylbenzophenone into the corresponding 2 : 3′-dicarboxylic acid by treatment with cuprous cyanide and pyridine (cf. de Diesbach, A., 1923, i, 804, etc.) was examined as an alternative. The results of the unsuccessful experiments illustrate the conditions under which the replacement of halogen by the cyano group takes place. *o*-Bromobenzophenone, when simply boiled with pyridine and cuprous cyanide for two days, affords *o-benzoylbenzonitrile*, m. p. 83·5°, b. p. 215—225°/20 mm., yielding anthraquinone when treated with sulphuric acid and *o*-benzoylbenzoic acid when submitted to the action of nitric acid, *d* 1·15, at 150°. 3-Chloro-4-methylbenzophenone (Heller, A., 1913, i, 631) is not attacked by cuprous cyanide

and pyridine even at 200°. When a mixture of benzoyl chloride and *o*-bromotoluene is treated with aluminium chloride a product is obtained which is stated by Mayer and Freund (A., 1922, i, 865) to be a mixture of 3- and 2-bromo-4-methylbenzophenones. Actually the substance, an oil of b. p. 195—210°/24 mm., interacts with cuprous cyanide and pyridine at 150° to yield an oil from which a small quantity of 3-*cyano*-4-*methylbenzophenone*, m. p. 106·5°, convertible into 4-benzoylphthalic acid, is obtained, yet if the crude nitrile be simultaneously oxidised and hydrolysed, and the impure dicarboxylic acid obtained purified by fractional crystallisation of its copper salt, the product is benzophenone-2 : 4-dicarboxylic acid. Thus migration of the bromine atom during the reaction with aluminium chloride, as described by Mayer and Freund, has taken place. When *o*-chlorobenzoyl chloride and *o*-chlorotoluene are treated with aluminium chloride in suspension in carbon disulphide, 2 : 3′-*dichloro*-4′-*methylbenzophenone*, m. p. 43·5°, b. p. 220—221°/24 mm., is obtained; the corresponding 3′-*chloro*-2-*bromo*-4′-*methylbenzophenone*, prisms, m. p. 50°, b. p. 229—231°/25 mm., is produced from *o*-bromobenzoyl chloride. When the first of these is treated with cuprous cyanide in pyridine at 200°, or the second at the b. p. of pyridine, 3′-*chloro*-2-*cyano*-4′-*methylbenzophenone*, m. p. 118·5°, is produced, yielding 3-chloro-4-methylbenzophenone-2′-carboxylic acid on hydrolysis. If the reaction with cuprous cyanide in pyridine be carried out at higher temperatures, complex products, still containing chlorine, are obtained; the chlorine atom therefore is not labile. *o*-Bromobenzoyl chloride and *o*-bromotoluene give a mixture of 2 : 3′- and 2 : 2′-*dibromo*-4′-*methylbenzophenones*, an oil, b. p. 240—243°/24 mm., solidifying eventually and then melting at 51°. When it is treated for two days with cuprous chloride and pyridine at 150° a mixture is obtained from which, if the pyridine be removed by distillation, a small amount of a *dinitrile*, m. p. 110°, can be separated; if however, the pyridine be removed by treating the mixture with hydrochloric acid, another product, possibly an *amide*, m. p. above 250°, is obtained. Both yield "phthaloylphthalic" acid when treated with dilute nitric acid at 200°. A further attempt to prepare phthaloylphthalic acid was based on the replacement, as above, of the chlorine atom in 3′-chloro-4′-methylbenzophenone-2-carboxylic acid, obtained from phthalic anhydride and *o*-chlorotoluene. Actually the chlorine atom remained in its place, but the carboxyl radical was detached, the product of the action of the cuprous cyanide and pyridine at 200° being 3-chloro-4-methylbenzophenone: substitution by the "phthaloyl" radical takes place therefore in the *para*-position to the methyl group, not to the chlorine atom as stated by Heller (*loc. cit.*). W. A. S.

Products of Decomposition of Benzaldoxime Peroxide. E. Parisi (*Gazzetta*, 1924, **54**, 485—490; cf. A., 1923, i, 579; this vol., i, 52).—When kept between filter-paper, benzaldoxime peroxide undergoes gradual decomposition, yielding α-benzaldoxime, benzaldehyde, benzoic acid, benzonitrile, dibenzenylazoxime, and the

N-benzoyl derivative of benzhydroxamic acid. A cold 10% solution of potassium hydroxide in alcohol also decomposes the peroxide, with formation of nitrogen, ammonia, nitrous acid, β-benzaldoxime, benzoic acid, hydroxamic acid, and dibenzenylazoxime.

T. H. P.

Colour and Molecular Geometry. II. Explanation of the Results of Chattaway and Clemo. J. Moir (*J. Chem. Soc.*, 1924, **125**, 1548—1551; cf. *ibid.*, 1923, **123**, 3041).—Alternate single and double bonds do not *per se* imply the possession by the substance of a "high" colour and the experimental results of Chattaway and Clemo are considered to be better accounted for by the orbit theory than by Hewitt's theory. In *p*-nitrobenzaldehyde phenylhydrazone, the orbit of the revolving electron surrounds the chain $NO_2 \cdot C_6H_4 \cdot CH{:}N \cdot N$. When CH_2 is substituted for the secondary amino group, the orbit contracts to include only the chain $NO_2 \cdot C_6H_4 \cdot CH{:}N$. Hence the wave-length of the characteristic absorption band is decreased and the substance exhibits a lower colour. In *p*-nitrophenylhydrazine and benzylidene-*p*-nitrobenzylamine, the orbit is assumed to surround the chains $NO_2 \cdot C_6H_4 \cdot N{:}N$ and $NO_2 \cdot C_6H_4 \cdot CH{:}N$, respectively. Hence the absorption bands of these substances should be, as in fact they are, in nearly the same position. With benzaldehyde-*p*-nitrophenylhydrazone the interfocal distance of the orbit is supposed to be the same as in *p*-nitrophenylhydrazine, but since the orbit now embraces the bulky benzylidene group, the periodic time of the electron is greater and hence the colour of the substance is higher. In general, the wave-length absorbed increases with the magnitude of the "loading." Results of the spectroscopic examination of some of the substances in the presence and absence of potassium hydroxide are given.

W. E. E.

Isomerism of the Oximes. XIX. Substituted Cinnamaldoximes. O. L. Brady and H. J. Grayson (*J. Chem. Soc.*, 1924, **125**, 1418—1421; cf. *ibid.*, 1922, **121**, 2098).—o-*Methoxycinnam*anti*aldoxime*, prepared by the action of hydroxylamine hydrochloride on the aldehyde suspended in sodium hydroxide solution, has m. p. 82°. The *acetyl* derivative also has m. p. 82°. It dissolves slowly in warm 2*N*-sodium hydroxide giving the sodium salt of the original oxime, thus establishing the *anti*-configuration of the latter. Thus *o*-methoxy- resembles the nitro-cinnamaldehydes, rather than the cinnamaldehydes. o-*Methoxycinnam*syn*aldoxime*, m. p. 135·5°, is obtained in the absence of alkali; *hydrochloride*, m. p. 142° (decomp.). The *acetyl* derivative, m. p. 77°, is formed instead of the usual nitrile by the action of acetic anhydride at 30°. *Benzoyl*-o-*methoxycinnam*anti*aldoxime*, m. p. 128°, is obtained from both the *syn*- and *anti*-oximes; it yielded only the *anti*aldoxime on hydrolysis (cf. T., 1922, **121**, 2098). The 2 : 4-*dinitrophenyl ether* of *o*-methoxycinnam*syn*aldoxime, m. p. 202° (decomp.), is obtained from the *anti*-oxime. m-*Nitrocinnam*syn*aldoxime*, m. p. 163°, was obtained when the *hydrochloride*, m. p. 175° (decomp.)

(formed on saturating a solution of the *anti*-oxime in hot benzene with hydrogen chloride), was treated with sodium hydroxide. Admixture with the *anti*-isomeride (m. p. 157°) caused a depression of the m. p.; its *acetyl* derivative, m. p. 98—100°, yielded *m*-nitrocinnamonitrile with alcoholic potassium hydroxide; this fixes its entity, as the *anti*-oxime under similar conditions gives an *acetyl* compound (m. p. 136°) from which the *anti*-oxime is regenerated. o-*Nitrocinnamsynaldoxime*, m. p. 138°, was obtained through its *hydrochloride*, m. p. 144° (decomp.), similarly to the *m*-nitro-compound. A purer compound, m. p. 140°, was obtained by Dunstan and Thole's method (P., 1911, **27**, 233). Its conversion into *o*-nitrocinnamonitrile proved its *syn*-configuration. p-*Nitrocinnamsynaldoxime* was not obtained in the pure state; its *hydrochloride*, m. p. 173° (decomp.), gave an oxime of m. p. 140° which depressed the m. p. (179°) of the *anti*-isomeride. A. C.

Preparation of Piperonal from *iso*Safrole and α-Homopiperonal from Safrole by Ozone. S. NAGAI (*J. Fac. Eng. Tokyo*, 1923, **13**, 185—192).—*iso*Safrole ozonide is readily prepared by passing ozonised air into a solution of *iso*safrole in perfectly dried solvents, *e.g.*, a mixture of chloroform, carbon tetrachloride or tetrachloroethane, and light petroleum. The ozonide decomposes spontaneously at the ordinary temperature, more readily on heating gently or in presence of water, with the production of considerable amounts of resinous matter. The best yield of piperonal is obtained when the ozonide is decomposed in the presence of reducing agents; thus, by employing a saturated aqueous solution of sodium hydrogen sulphite a yield of 85% of theory was produced.

Safrole ozonide is obtained in a similar manner, but owing to its lesser solubility mixed solvents are not required. The best method of decomposition of the ozonide consists in the gradual addition of zinc dust and water to its solution in glacial acetic acid, when yields of 60—65% of α-homopiperonal result. The aldehyde has b. p. 131—133°/8 mm., d_4^{15} 1·2654, n_D^{15} 1·5547; *oxime*, m. p. 109°, *semicarbazone*, m. p. 175—176°, and *phenylhydrazone*, m. p. 176°. C. J. S.

Photochemical Reactions in Solutions of the Alkali Halides in Acetophenone. J. L. R. MORGAN, O. M. LAMMERT, and R. H. CRIST (*J. Amer. Chem. Soc.*, 1924, **46**, 1170—1178).—Pure acetophenone is decomposed by the light from a quartz-mercury lamp, apparently with the production of benzoic acid. A yellow colour appears, possibly due to the formation of condensation products, and the specific electrical resistance decreases. In the dark this again increases, but the yellow colour continues to deepen. The presence of water accelerates the reaction. A solution of sodium iodide in acetophenone increases in resistance in the light, iodine is liberated, and a fine, white deposit, which appears to be sodium benzoate, is formed. There are breaks in the curves showing variation of resistance with time, thus indicating that concurrent or overlapping reactions are taking place in the solution. A scheme

of combined thermal and photochemical reactions has therefore been put forward as a possible explanation of the changes observed.

The effective wave-lengths for the reactions in glass vessels are 300 $\mu\mu$ and 400 $\mu\mu$. The effects are more pronounced and differ somewhat in character in quartz vessels, indicating that the shorter wave-lengths are more effective for at least some of the reactions.

M. S. B.

Beckmann's Rearrangement. XII. Catalytic Action of Reduced Copper on Acetophenoneoxime. S. YAMAGUCHI (*Mem. Coll. Sci. Kyoto*, 1924, **7**, 281—285).—Acetophenoneoxime, when passed with hydrogen over reduced copper at 200°, yielded benzoic acid, ammonium benzoate, α-phenylethylamine, αα-diphenylethylamine, benzonitrile, acetophenone, and unchanged oxime.

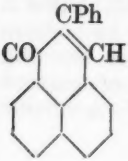
F. G. M.

Mono- and Di-chloro-1-ketotetrahydronaphthalene. TETRALIN G.M.B.H. and W. RIEBENSAHM (D.R.-P. 377587; from *Chem. Zentr.*, 1924, i, 956).—By chlorination of 1-ketotetrahydronaphthalene are obtained *dichloro-1-ketotetrahydronaphthalene*, m. p. 75—76°, and *monochloro-1-ketotetrahydronaphthalene*, m. p. 45°. G. W. R.

Changes in State of Aggregation and Polymorphism. IV. Formation of Metastable Benzophenone. K. SCHAUM and K. ROSENBERGER (*Z. anorg. Chem.*, 1924, **136**, 329—336).—The addition of hydrogen chloride to either the rhombic α or the monoclinic, metastable, β form of benzophenone results in an equilibrium being established between the two modifications, which, at low temperatures, corresponds with the formation of the eutectic mixture. The hydrogen chloride acts as a catalyst in this change probably by forming an unstable additive product with the benzophenone since, on passing the gas into the molten compound, the latter develops a bright grass-green colour. This view is strengthened by the fact that compounds, such as metallic chlorides, which are known to give additive products with benzophenone also accelerate the change from the stable α to the metastable β form. Benzophenone forms eutectic mixtures with 70 and 30 mol.% of diphenylamine (m. p. 29·5° and 25° respectively), with 39 mol.% of benzhydrol (m. p. 23°), with 24 mol.% of triphenylmethane (m. p. 33°), with 10 mol.% of 4 : 4′-dichlorobenzophenone (m. p. 43°), and with 26 mol.% of ditolyl ketone (m. p. 34°). Of a number of substituted benzophenones tested only *p*-ditolyl ketone exhibited polymorphism.

A. R. P.

Vat Dyes. KALLE U. CO. (D.R.-P. 384982; from *Chem. Zentr.*, 1924, i, 1111).—*Potassium* 1-*aldehydonaphthalene*-8-*carboxylate* condenses with phenylacetonitrile to give 1-β-*cyanostyrylnaphthalene*-8-*carboxylic acid*, m. p. 162—165°, which is converted by sulphuric acid into 2-*phenylperinaphthindone* (annexed formula), m. p. 142°. The last is converted by fusion with potassium hydroxide into a blue vat dye.



G. W. R.

Aryl 4-Hydroxynaphthyl Ketones. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Swiss Pats. 100366, 100367, 100368, 100369, 100370, and 100371; from *Chem. Zentr.*, 1924, i, 2204—2205; cf. this vol., i, 174—175).—The following new compounds are mentioned: o-*chlorophenyl* 4-*hydroxynaphthyl ketone*, m. p. 216°; p-*chlorophenyl* 4-*hydroxynaphthyl ketone*, m. p. 210°; 2 : 4-*dichlorophenyl* 4-*hydroxynaphthyl ketone*, m. p. 222°. G. W. R.

An Aryl Hydroxynaphthyl Ketone. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Swiss Pat. 101402; from *Chem. Zentr.*, 1924, i, 2205; cf. preceding abstract).—2-*Benzoyl*-1-*naphthol*-4-*sulphonic acid* is obtained by the action of benzotrichloride on sodium 1-naphthol-4-sulphonate. G. W. R.

Residual Affinity and Co-ordination. XVIII. Interaction of Zirconium Salts and β-Diketones. G. T. MORGAN and A. R. BOWEN (*J. Chem. Soc.*, 1924, **125**, 1252—1261).—The method developed by Biltz and Clinch (A., 1904, i, 715) to form zirconium acetylacetone in aqueous solution proved impracticable when tried with homologues of acetylacetone, whilst the higher aliphatic diketones and sodium benzoylacetone (which produced zirconyl bisbenzoylacetone) also gave unsuccessful results. In place of this, a general reaction was obtained between anhydrous zirconium tetrachloride and the β-diketones in dry chloroform or benzene, whereby three chlorine atoms were replaced. *Zirconium trisdibenzoylmethane chloride*, so obtained, is very stable in the dry state and gives crystalline double salts such as the *ferrichloride*, *chloroaurate*, and *chloroplatinate*. *Zirconium trisbenzoylacetone chloride* is less stable, whilst the *trisacetylacetone chloride* is the most readily hydrolysable member of the series. A. COUSEN.

Action of Selenium Tetrachloride on Di- and Tri-ketones. Selenium Phenylacetyl- and β-Phenylpropionyl-acetones. G. T. MORGAN and C. R. PORTER (*J. Chem. Soc.*, 1924, **125**, 1269—1277).—The copper derivative of ω-phenylacetylacetone reacts readily with selenium tetrachloride producing mainly the dimeric *selenium ω-phenylacetylacetone* and 3-*chloro*-ω-*phenylacetylacetone*. β-Phenylpropionylacetone similarly reacts to give *selenium* β-*phenylpropionylacetone*. These compounds, reduced with hydriodic acid, give *diselenium bis*-ω-*phenylacetylacetone* and *bis*-β-*phenylpropionylacetone*, respectively, anhydrous hydrocyanic acid also reacting to give *cyanoselenium ω-phenylacetylacetone* and the β-phenylacetylacetone. The products are all enolic, the reduction compounds being orange-coloured oils which are also obtained as by-products of the original condensations. Selenium tetrachloride reacts with the barium salt of diacetylacetone chiefly as a dehydrating and chlorinating agent, the chief derivative being 3 : 5-*dichloro*-2 : 6-*dimethylpyrone*, white needles, m. p. 148—150°, whilst much free selenium is also obtained. This pyrone with barium hydroxide affords an enolic substance, probably 3-*chloro*-5-*acetyl*-4-*hydroxy*-2-*methylfuran*, m. p. 83—84°. Chlorination of barium diacetylacetone yields *trichlorodiacetylacetone*,

$$COMe{\cdot}CCl_2{\cdot}CO{\cdot}CHCl{\cdot}COMe,$$

m. p. 105—106°. A. COUSEN.

1-Chloro-2-acylamidoanthraquinones. E. KOPETSCHNI (D.R.-P. 376471; from *Chem. Zentr.*, 1924, i, 967).—β-Acylamidoanthraquinones are chlorinated by means of sulphuryl chloride in an indifferent solvent. 1-*Chloro*-2-*acetamidoanthraquinone* has m. p. 241°; 1-*chloro*-2-p-*toluenesulphamidoanthraquinone*, green needles, m. p. 204—205° (decomp.); *sodium* salt of the latter,

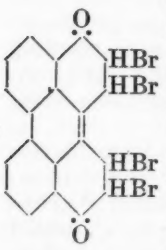
$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_2Cl(NNa\cdot SO_2\cdot C_7H_7),$$

red crystals. G. W. R.

Sodium Alizarate and Alumina. F. S. WILLIAMSON (*J. Phys. Chem.*, 1924, **28**, 891—892).—Experiments are described from which the author infers that no definite aluminium alizarate is formed when aluminium hydroxide and sodium alizarate are mixed, contrary to the supposition of Liechti (*J. Soc. Chem. Ind.*, 1886, **5**, 523). S. B.

Action of Thionyl Chloride on Hydroxyanthraquinones. I. Thionylalizarin. A. GREEN (*J. Chem. Soc.*, 1924, **125**, 1450—1451).—*Thionylalizarin*, $C_{14}H_6O_2<\begin{matrix}O\\O\end{matrix}>SO$, prepared by the action of boiling thionyl chloride on dry alizarin, forms yellow crystals, m. p. 171—172°; the colour changes to orange-yellow after a few hours in a sealed tube, but the m. p. and sulphur content remain unchanged. The substance is stable in dry air, but converted into alizarin by moisture. The colours of its solutions in aqueous sodium hydroxide and concentrated sulphuric acid are the same as those of alizarin. *Alizarin monoacetate*, m. p. 201—202°, is formed on boiling thionylalizarin with glacial acetic acid, and the *diacetate*, m. p. 185°, on using acetic anhydride. A. C.

Perylene and its Derivatives. IV. A. ZINKE and H. SCHÖPFER [with G. MÜLLER, R. SABATHY, M. SCHNEIDER, and W. SPITZY] (*Monatsh.*, 1924, **44**, 365—370).—Careful bromination of perylenequinone in the cold yields, besides dibromoperylenequinone (A., 1920, i, 541), 1 : 2 : 11 : 12-*tetrabromotetrahydroperylenequinone* (annexed formula), bright yellow needles, rapidly darkening, which readily loses hydrogen bromide, giving dibromoperylenequinone. On chlorination in nitrobenzene on the water-bath, perylenequinone similarly yields 1 : 2 : 11 : 12-*tetrachlorotetrahydroperylenequinone*, which is more stable than the tétrabromo compound, but at about 265°, or by crystallisation from aniline or heating with pyridine, is converted into *dichloroperylenequinone*, which dyes cotton pure yellow. Nitration of perylenequinone with concentrated nitric acid in boiling acetic acid solution gives, besides the mononitro derivative previously described (Zinke and Unterkreuter, *loc. cit.*), a *dinitroperylenequinone*, $C_{20}H_8O_2(NO_2)_2$, which dyes cotton dull violet. On reduction with alkaline sodium hyposulphite, the mononitro compound yields *aminoperylenequinone*, $C_{20}H_9O_2\cdot NH_2$,



and the dinitro compound gives diaminoperylenequinone, $C_{20}H_{12}O_2N_2$; *diacetyl* derivative; *dibenzoyl* derivative, needles.

R. B.

Perylene and its Derivatives. V. A. ZINKE and A. PONGRATZ (*Monatsh.*, 1924, **44**, 379—382).—Perylenequinone stands between α-naphthaquinone and anthraquinone in its quinonoid properties, and is much more stable than *pp'*-diphenoquinone, from which it is genetically derived (cf. Willstätter and Kalb, A., 1905, i, 361). It gives no reaction with aqueous hydriodic acid in nitrobenzene solution or with guaiacum resin or hæmatoxylin in alcoholic solution. With phenylhydrazine and hydroxylamine at higher temperatures, it yields no hydrazone or oxime, but apparently undergoes reduction. It does not react with sulphurous acid, but is reduced by stannous chloride in acetic acid solution. A solution of perylenequinone in acetic acid, on the addition of potassium iodide, gives after some minutes a reaction for free iodine; *p*-benzoquinone gives an immediate reaction, α-naphthaquinone after a few seconds, and anthraquinone an uncertain reaction after 30 to 35 mins. The solution of perylenequinone gradually deposits brownish-violet needles of *perylenequinhydrone*, $C_{40}H_{20}O_4$. *Perylenequinol*, $C_{20}H_{12}O_2$ (cf. Zinke and Unterkreuter, A., 1920, i, 541), obtained by reduction of perylenequinone with potassium iodide and red phosphorus in acetic acid solution, or with zinc dust and acetic acid, shows an intense yellowish-green fluorescence in solution and readily oxidises in air to a quinhydrone.

R. B.

Aminoperylenequinones. H. PEREIRA (Brit. Pat. 199721).—Mononitro-, dinitro-, and *bromodinitro*-perylenequinones afford, on reduction with hot alkaline sodium hyposulphite, *monoamino-*, *diamino-*, and *bromodiamino-perylenequinones*, respectively, all of which form dark needles and dye cotton in brown to violet shades (cf. A., 1920, i, 542, and Brit. Pat. 199720). F. G. W.

Attempt to Synthesise Dinaphthanthracenediquinone [Dinaphthanthradiquinone]. H. DE DIESBACH and L. CHARDONNENS (*Helv. Chim. Acta*, 1924, **7**, 609—613).—When "phthaloylphthalic anhydride" (the anhydride of benzophenone-2 : 3' : 4'-tricarboxylic acid; Limpricht, A., 1900, i, 599) and benzene are treated with aluminium chloride, *1 : 5-dibenzoylbenzene-2 : 2'-dicarboxylic acid*, m. p. 177—180°, is produced. This undergoes further condensation when treated with strong sulphuric acid on the water-bath, yielding *2-benzoylanthraquinone-2'-carboxylic acid*,

$$CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}C_{14}H_7O_2,$$

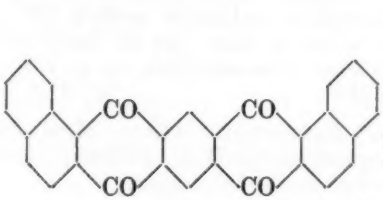
yellow prisms giving a bottle-green "vat" with sodium hydrosulphite, soluble in benzene, m. p. 218° after sintering at 198°, together with a little 2-benzoylanthraquinone-3-carboxylic acid, insoluble in benzene and giving a reddish-brown "vat" (cf. Fairbourne, T., 1921, **119**, 1580). The former was also prepared by condensing phthalic anhydride with 9 : 10-dihydroanthracene, much anthroylbenzoic acid or similar compounds being formed as by-products (cf. Schaarschmidt, A., 1916, i, 381); further condensation

to dinaphthanthradiquinone was not satisfactorily brought about. 1-*p*-Methylbenzoyl-5-benzoylbenzene-2 : 2′-dicarboxylic acid undergoes a similar condensation, not wholly decomposition, as stated by Limpricht (*loc. cit.*), when heated with strong sulphuric acid, yielding 2 : 6-*benzoylmethylanthraquinone-2′-carboxylic acid*, m. p. 213°. (Cf. this vol., i, 1074.) W. A. S.

Dibenzoylxylenes and Dinaphthanthradiquinones. II. H. DE DIESBACH and L. CHARDONNENS (*Helv. Chim. Acta*, 1924, **7**, 614—618; cf. A., 1923, i, 804).—When α-cumidic acid is treated with sulphuric acid and potassium nitrate at 50° it yields solely a mononitro derivative, 2-*nitro*-m-*xylene*-4 : 6-*dicarboxylic acid*, m. p. 294°, the *dimethyl* ester of which has m. p. 143·5—144·5°. Reduction of the nitro-acid affords the corresponding *amino-acid*, m. p. 305—306°, the *dimethyl* ester of which has m. p. 95·5—97°. By the action of phosphorus pentachloride followed by aluminium chloride, on a solution of the nitrocumidic acid in benzene 2-*nitro*-4 : 6-*dibenzoyl*-m-*xylene* is obtained, m. p. 126—127°. This compound is oxidised by the action of nitric acid, *d* 1·15, at 200°, affording 2-*nitro*-4 : 6-*dibenzoyl*isophthalic *acid*, m. p. 235—238°, which, by treatment with sulphuric acid at 200°, is converted into 6-*nitro*-5 : 7 : 12 : 14-*dinaphthanthradiquinone*, subliming without melting at 285—290°. W. A. S.

Some Derivatives of Dinaphthanthradiquinone and the Synthesis of Dinaphthalinoanthradiquinone. H. DE DIESBACH and V. SCHMIDT (*Helv. Chim. Acta*, 1924, **7**, 644—653; cf. A., 1923, i, 804; Philippi, A., 1923, i, 576; 1913, i, 627).—Pyromellitic anhydride and toluene react (Philippi, *loc. cit.*) in presence of aluminium chloride to give a mixture of much 4 : 6-di-*p*-toluoyl*iso*-phthalic acid, the *methyl* ester of which has m. p. 194—195°, and a little 2 : 5-di-*p*-toluoylterephthalic acid, *methyl* ester, m. p. 203°, less soluble in alcohol than its isomeride. Philippi's conclusions (*loc. cit.*) as to the possibility of further condensation taking place are now shown to be unfounded : when the crude mixture of the above acids, or the first alone, is treated with 90% sulphuric acid at 180°, a poor yield of 2 : 10-*dimethyl*-5 : 7 : 12 : 14-*dinaphthanthradiquinone* is obtained, not melting below 350°, which, like its congeners described previously and below, yields a brown "hyposulphite vat" which turns blue on exposure to air. The isomeric 2 : 9-*dimethyl*-5 : 7 : 12 : 14-*dinaphthanthradiquinone* was also obtained. Similarly, pyromellitic anhydride and *o*-chlorotoluene yield (82% of theory) 4 : 6-*di*-3′-*chloro*-p-*toluoyl*isophthalic *acid*, m. p. 302°, which affords a *methyl* ester, m. p. 234—235°, and 2 : 5-*di*-3′-*chloro*-p-*toluoylterephthalic acid*, m. p. 315°, *methyl* ester, m. p. 241°. When the crude mixture of acids is heated with 90% sulphuric acid at 180°, 40% of the theoretical yield of the corresponding dinaphthanthradiquinones is obtained. The two substances are separated by fractional extraction with nitrobenzene. Neither interacts with toluidine in presence of sodium acetate and a copper salt; the chlorine atoms therefore are not adjacent to

the carbonyl groups. 3 : 9-*Dichloro*-2 : 10-*dimethyl*-5 : 7 : 12 : 14-*dinaphthanthradiquinone* decomposes at 320°, whilst 3 : 10-*dichloro*-2 : 9-*dimethyl*-5 : 7 : 12 : 14-*dinaphthanthradiquinone* remains unmelted at 350°. From *p*-chlorotoluene, in like manner, 4 : 6-*di*-3′-*chloro*-o-*toluoyl*isophthalic *acid*, m. p. 313°, giving a *methyl* ester, m. p. 164—165°, was obtained, together with 2 : 5-*di*-3′-*chloro*-o-*toluoylterephthalic acid*, m. p. 325°, *methyl* ester, m. p. 182°. The first of these, or the crude mixture, as it contains only a very small proportion of the second acid, yields 4 : 8-*dichloro*-1 : 11-*dimethyl*-5 : 7 : 12 : 14-*dinaphthanthradiquinone*, m. p. 270° (decomp.). When aluminium chloride is added to a solution of pyromellitic anhydride, naphthalene, and benzene at 30°, and the mixture heated during 10 hours at 30—60°, two acids are obtained which may be separated from one another by fractional crystallisation from water, acetic acid, and alcohol, used in succession. 4 : 6-*Di*-α-*naphthoyl*isophthalic *acid* has m. p. (when anhydrous) 302°; its *methyl* ester has m. p. 205°. 2 : 5-*Di*-α-*naphthoylterephthalic acid* has m. p. 316°. For effecting the further condensation to the anthradiquinone derivatives, sulphuric acid cannot be used, because sulphonation takes place (some products of the action are described); but the reaction can be brought about by heating the acid with phosphorus pentoxide at 300—310°. If the crude mixture of acids be used, a product is obtained which may be separated into its two components by fractional extraction with acetic acid and crystallisation from nitrobenzene; or the two isomerides may be prepared each from its appropriate acid. In this way 1 : 2 : 10 : 11-*dibenzo*-5 : 7 : 12 : 14-*dinaphthanthradiquinone* (syn-biangular-2 : 3 : 6 : 7-*dinaphthalino*-1 : 4 : 5 : 8-*anthradiquinone*, Stelzner's nomenclature), brick-red needles, decomposing without melting at 320° (I), and the corresponding 1 : 2 : 8 : 9-compound (anti-biangular-2 : 3 : 6 : 7-*dinaphthalino*-1 : 4 : 5 : 8-*anthradiquinone*), somewhat paler needles,



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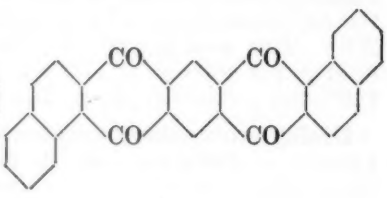


(II.)

unaltered even at 360° (II), are obtained. Both substances yield a violet "vat" with sodium hyposulphite, the colour changing to green and eventually to orange, on exposure to air.

When tetrahydronaphthalene is used instead of naphthalene, the condensation takes place smoothly and appears to result in the production of only one of the possible isomerides, *viz.*, 4 : 6-*di*-β-ar-*tetrahydronaphthoyl*isophthalic *acid*, m. p. 289—290°. Attempts to convert this compound into an anthradiquinone failed, oxidation taking place at high temperatures. W. A. S.

Action of Tetrachloro- and Tetrabromo-phthalic Acids on Turpentines. New Method of Preparing Camphols and *d*- and *l*-Camphor. A. HALLER (*Compt. rend.*, 1924, **178**, 1933—1937; cf. Bouchardat and Lafont, A., 1892, 199; Bouchardat and Tardy, A., 1895, i, 673).—Bornyl and fenchyl esters may be prepared by the action of acids on terpenes provided that the acid used is soluble in the terpene. Tetrahalogenophthalic acids fulfil this condition and react with pinenes yielding bornyl, *iso*bornyl, and fenchyl esters from which mixtures of these alcohols may be obtained on hydrolysis. Both the yield and the relative proportion of esters obtained depend on the temperature and also on the duration of the reaction, and details of experiments carried out with turpentine from *Pinus maritima* and *P. halepensis* and tetrachloro- and tetrabromo-phthalic acids under different conditions are given.

H. J. E.

The Camphor and Camphenilone Series. Reply to L. Ruzicka. S. NAMETKIN (*Annalen*, 1924, **438**, 202).—Explanatory (cf. this vol., i, 64). W. A. S.

The Camphenilane Series. S. NAMETKIN (*Annalen*, 1924, **438**, 185—201).—A review of earlier work (cf. A., 1915, i, 699) with particular reference to the results of Komppa and Roschier (A., 1922, i, 1167). The compound described as β-nitrocamphenilane (Nametkin and Chuchrikova, A., 1915, i, 701) is now termed α-nitrocamphenilane, whilst the 6-nitro- is now the 2-nitro derivative. The *apo*fenchocamphoric acid previously described (m. p. 144·5—145°) is now shown to be cis-apo*fenchocamphoric acid*. Various salts are briefly described. The solubility of the acid in water is 0·72 g. per 100 c.c. at 19°. With acetyl chloride in the cold, it yields the *anhydride*, m. p. 136—137°. The acid affords a *monoanilide*, m. p. 155—157°, and a *dianilide*, m. p. 148—150°. trans-apo*Fenchocamphoric acid*, m. p. 147—148°, is obtained when the *cis*-variety is heated with hydrochloric and acetic acids at 180—200°. This acid is more soluble in water than the *cis* isomeride (0·81 g. per 100 c.c. at 17°). It yields a *monoanilide*, m. p. 138—142°, and a *dianilide*, m. p. 215—216°. W. A. S.

Dialkylaminoalkylcamphors. FARBWERKE VORM. MEISTER, LUCIUS, U. BRÜNING, and M. BOCKMÜHL (D.R.-P. 376348; from *Chem. Zentr.*, 1924, i, 1103).—*Diethylaminoethylcamphor*,

$$C_8H_{14}<\begin{matrix}CH\cdot CH_2\cdot CH_2NEt_2\\ |\\ CO\end{matrix},$$

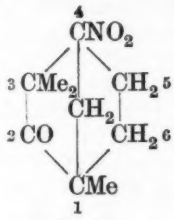
is an oil; the *hydrochloride* has m. p. 145°. *Dimethylaminoethylcamphor* is a yellow oil, b. p. 135—150°/10 mm.; *hydrochloride*, m. p. 231°. G. W. R.

Origin of Fenchol in Bouchardat and Lafont's Reaction. M. DÉLÉPINE (*Compt. rend.*, 1924, **178**, 2087—2089; cf. Bouchardat and Lafont, A., 1892, 199).—The action of benzoic and trichloroacetic acids on *d*-pinene and on *l*-pinene, respectively, results in formation of both fenchol and borneol derivatives in all four cases.

H. J. E.

Nitrofenchones and some of their Reactions. S. NAMETKIN (*J. pr. Chem.*, 1924, [ii], **108**, 29—45).—By the action of nitric acid on fenchone, a *sec.*- and *tert.*-nitrofenchone were obtained by Konovalov (A., 1904, i, 257). These products have been further investigated.

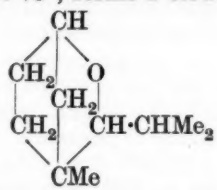
[With (Miss) W. CHOCHRJAKOV.]—The *tert.*-nitrofenchone has the annexed formula, instead of that given by Konovalov (*loc. cit.*).

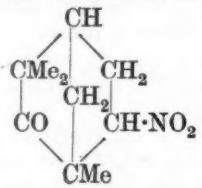


The reduction product with tin and hydrochloric acid is not a hydroxyfenchone, but a *diketone*, $C_{10}H_{16}O_2$, a colourless oil with a pleasant odour, b. p. 126·5—127°/11 mm., d_4^{20} 1·0028, n_D^{20} 1·4641 $[\alpha]_D$ −46·59° in alcohol. It forms a *disemicarbazone*, $C_{10}H_{16}(:N\cdot NH\cdot CO\cdot NH_2)_2$, decomp. 220°, and a *dioxime*, m. p. 123—124°. The diketone is reduced by sodium and alcohol to a *glycol*, $C_{10}H_{18}(OH)_2$, b. p. 151—152°/11 mm., $[\alpha]_D$ +44·54° in alcohol, giving a *diacetate*, b. p. 152—153°/12 mm., d_4^{20} 1·0189, n^{20} 1·4530. The dry glycol is converted by warm sulphuric acid into the *oxide*, $C_{10}H_{18}O$, b. p. 171—172°/749 mm., d_4^{20} 0·8985, n^{20} 1·4478; its formation is accompanied by that of other products. The formation of the diketone from the *tert.*-nitrofenchone involves the scission of one ring. The readiness with which the glycol forms an anhydride renders extremely probable the formula $\begin{matrix}CO\text{—}CH_2\\ |\\ CH_2\cdot CH_2\end{matrix}>CMe\cdot CO\cdot CHMe_2$ for the diketone, scission having occurred between carbon atoms 3 and 4 of the fenchone ring. The oxide then has the formula I.

[With (Miss) K. LÜBOVZOV.]—The *sec.*-nitrofenchone, m. p. 88°, $[\alpha]_D$ −42·88° in benzene, is a true nitro compound. With bromine in alkaline solution, it forms *bromonitrofenchone*, $C_{10}H_{14}O\cdot BrNO_2$, m. p. 53°. The only product of the acid reduction of *sec.*-nitrofenchone is a *ketonic acid*, $C_9H_{15}O\cdot CO_2H$, which begins to melt at 73°, forms a cloudy liquid at 76° and clears at 79—80°;

(I.)





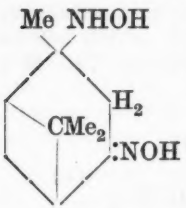
(II.)

it forms a *semicarbazone*, decomp. 188°. This acid possibly has the structure $\begin{matrix}CHMe\cdot CH_2\\ |\\ CO\text{—}CMe_2\end{matrix}>CH\cdot CH_2\cdot CO_2H$, and is related to *iso*-camphoronic acid which, with αα-dimethyltricarballylic acid, is formed during the nitration of fenchone. *sec.*-Nitrofenchone probably has formula II.

By the action of nitric acid on camphenilone, two products are obtained, a liquid and crystals, m. p. 90—92°, apparently isomeric *nitro* derivatives. As a by-product, *iso*camphoronic acid was identified, and its formation supports the accepted formula for camphenilone. E. H. R.

Preparation of Monoalkylpulegones. A. HALLER and (MME.) P. RAMART (*Compt. rend.*, 1924, **179**, 120—122).—Pulegone in ethereal solution is treated first with an equimolecular quantity of powdered sodamide and then with the theoretical quantity of the requisite alkyl iodide, the alkylpulegone being finally isolated by distillation. The yields are low, owing chiefly to intermolecular condensation of the pulegone under the influence of the sodamide. The following compounds are described. *Methylpulegone*, b. p. 114°/19 mm., d_4^{23} 0·9256, $[\alpha]_D^{15}$ −26·24°, *semicarbazone*, liquid; *ethylpulegone*, b. p. 117—121°/20 mm., d_4^{15} 0·9315, $[\alpha]_D^{15}$ −25·12°, *semicarbazone*, m. p. 216°; n-*propylpulegone*, b. p. 127—131°/20 mm., d_4^{15} 0·9476, $[\alpha]_D^{15}$ −22·10°, *semicarbazone*, m. p. 170°; iso*butylpulegone*, b. p. 128—132°/20 mm., d_4^{15} 0·9225, $[\alpha]_D^{15}$ −18·28°, *semicarbazone*, liquid; *allylpulegone*, b. p. 129—133°/20 mm., d_4^{15} 0·9399, $[\alpha]_D^{15}$ −27·86°, odour resembling that of vetiver and ionone, *semicarbazone*, m. p. 196°. F. G. M.

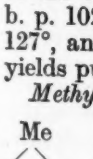
Chemistry of the Terpene Group. I. Formation and Transformations of Verbenone and Verbenol from Turpentine. H. WIENHAUS and P. SCHUMM (*Annalen*, 1924, **439**, 20—48).—The auto-oxidation of Grecian turpentine in air, very slow under ordinary conditions, but much more rapid in sunlight and in the presence of an appropriate catalyst, yields verbenol and verbenone. A resin acid, $C_{20}H_{30}O_2$, known to be formed by the oxidation of turpentine, was isolated. In the oxidation of pinene by means of colloidal osmium and oxygen (cf. Willstätter and Sonnenfeld, A., 1913, i, 1200) α-pinene takes up 1 mol. of oxygen and, from the acid, viscous liquid produced, *d*-verbenone is isolated; oxime, m. p. 119—120° (cf. Blumann and Zeitschel, A., 1913, i, 495, give m. p. 115°), semicarbazone, m. p. 208° (decomp.). Excess of hydroxylamine yields the *hydroxylamino-oxime* (annexed formula), decomp. 165° (170° with rapid heating). Catalytic reduction of verbenoneoxime using palladium and hydrogen gives only a resinous product when 1 mol. of hydrogen is used, but with 3 mols. the product is verbanylamine, which is obtained by similar reduction of verbanoneoxime. By the action of 15% hydrogen peroxide in methyl-alcoholic sodium hydroxide solution, *d*-verbenone yields an *oxide*, b. p. 115°/16 mm., m. p. 6·5°, d_4^{20} 1·0561, n_D^{20} 1·48312, *semicarbazone*, m. p. 220° (decomp.). The formation of this oxide is a typical reaction for αβ-unsaturated ketones and together with the formation of the hydroxylamine-oxime proves that the double bond in the ring is conjugated with the keto group. The presence of a CH_2 group adjacent to the carbonyl group follows from the easy formation of an oximino derivative. Oxidation of verbenone and its oxime with ozone yields pinonic acid. Catalytic reduction (with palladium and hydrogen) of verbenone yields *d*-verbanone, which on reduction with sodium yields verbanol, b. p. 100°/13 mm., m. p. 58°, and a *pinacone*, m. p. 211—212°, b. p. 250—254°/22 mm. Verbanone yields a *hydrazone*, m. p. 27°, b. p. 146°/22 mm., d_4^{27} 0·986, n_D^{27} 1·51743,



which at 140—160° yields pinane; *semicarbazone*, decomp. 230°; oxime, m. p. 88° (Blumann and Zeitschel, *loc. cit.*, give 77—78°), *hydrochloride*, m. p. 131°. Dilute sulphuric acid, (1 : 5, 1 : 2) regenerates the ketone from its oxime, but concentrated acid (1 : 1) yields a little *nitrile*, b. p. 230—236°, which is also obtained from the oxime by treatment with phosphorus pentoxide. Reduction of the nitrile with either sodium and alcohol, aluminium amalgam and moist ether, or platinum black and hydrogen, yields *verbanylamine*, b. p. 113—114°/20 mm., 211°/750 mm., d_4^{20} 0·9184, n_D^{20} 1·48125; *hydrochloride*, decomp. 245—250°; *nitrate*, decomp. 200°; *oxalate*, m. p. 131°. Concentrated mineral acids resinify verbanone, but by the action of 12% hydrochloric acid or 20% sulphuric acid it is converted into Δ^1-*o*-menthen-3-one, which on reduction by means of palladium black yields *o*-menthan-3-one. Reduction of verbanone by means of amalgamated zinc and 12% hydrochloric acid yields *o*-menthane, b. p. 169—170°/752 mm., d_4^{20} 0·8297, n_D^{20} 1·45649, $[\alpha]_D$ +14·9°, identical with that synthesised from *o*-tolyldimethylcarbinol (cf. Sabatier and Murat, A., 1913, i, 255). Fission of the six membered ring, leaving the four-membered ring intact, is accomplished by the action of sodamide and *iso*amyl nitrite on verbanone, which yields an *oximino* derivative, m. p. 140°. This on treatment with acetic anhydride yields the isomeric *imide* of the pinocamphoric acid obtained by Wallach and Engelbrecht (A., 1906, i, 684), m. p. 96°. Hydrolysis by means of dilute sodium hydroxide of either the oximino derivative or the imide yields the corresponding *amide*, m. p. 120°, which, unlike the amide of camphoric acid, is stable towards dilute alkalis. By means of the Grignard reaction verbanone yields the tertiary alcohol, *methylverbanol*, m. p. 187°, which yields a stable chromate sensitive to light. On distillation at ordinary pressure, or by heating with anhydrous oxalic acid the tertiary alcohol yields *homopinene*, b. p. 184—188°/748 mm., d_4^{20} 0·8538, n_D^{20} 1·47144, which shows considerable exaltation of molecular refraction. Like camphor, verbanone yields a white *additive* product on treatment with sodamide and carbon dioxide in anhydrous ether, which on acidification regenerates carbon dioxide and verbanone and is therefore an ester of the acid $C_8H_{14}<\begin{matrix}CH\\ \|\\ CO\cdot CO_2H\end{matrix}$.

The isolation of pure verbenol from the fraction, b. p. 130—150°/17 mm., of the product of auto-oxidation of Grecian turpentine is much more difficult. Catalytic reduction (palladium and hydrogen) of the crude verbenol yields crude verbanol, of which a fraction, b. p. 102°/20 mm., d_{20} 0·940, n_D^{20} 1·47618, forms a phthalate, m. p. 127°, and on oxidation by means of chromic acid and acetic acid yields pure verbanone.

Methyl verbanylxanthate, b. p. 100—110°/23 mm., on distillation yields a *hydrocarbon*, b. p. 156—159°/748 mm., d_4^{20} 0·8604, n_D^{20} 1·46672, $[\alpha]_D$ −6·22°, which is not α-pinene, since it yields a viscous red oil and not pinene hydrochloride on treatment with hydrochloric acid, and is probably δ-pinene (I), the preparation of which by the exhaustive methylation of verbanylamine (II) is in pro-



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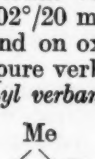


(II.)

gress. Crude verbanol is probably a mixture of stereoisomeric alcohols. J. W. B.

Turpentines. G. DUPONT (*Ann. Chim.*, 1924, [x], **1**, 184—274).—An amplification and extension of previous work (cf. Dupont, A., 1922, i, 357; Vèzes and Dupont, A., 1922, i, 1042; Dupont, A., 1922, i, 1043; Dupont and Desalbres, A., 1923, i, 812; Dupont and Brus, A., 1923, i, 934; Dupont and Desalbres, A., 1923, i, 1215). Indian turpentine is characterised by its large proportion of Δ^3-carene and of longifolene, a sesquiterpene, whilst the percentages of pinene (24·8) and nopinene (9·7) are relatively small. The purest specimens of pinene obtained by the author from Aleppo turpentine had d^{15} 0·8620, n_D^{12} 1·4650, and $[\alpha]_D$ +48·08°, the velocity of crystallisation at −75° being 34 mm./min.; whilst the corresponding figures for pinene from Bordeaux turpentine were 0·8620, 1·4649, −46·65°, and 16·3 mm./min. The values for nopinene are 0·8740, 1·4872, and 196·5 mm./min. A study of the chemical properties of pinene and nopinene leads to the generalisation that if these two substances, by fixation of two atoms or groups, yield the same derivative, one of the entering groups must be a hydrogen atom. The following constants are given for Δ^3-carene: b. p. 170°, 70°/10 mm., d^{15} 0·8668, n_D^{25} 1·4675 (cf. Simonsen, T., 1920, **117**, 570). Hydrochloric acid acts on this substance, yielding a mixture of sylvestrene and dipentene hydrochlorides; potassium permanganate oxidises it to carene glycol, thence to *trans*-caronic acid. H. J. E.

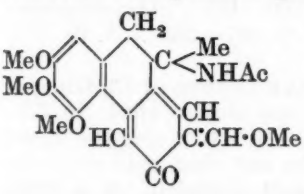
Transformations of Pinene by Acids. M. DELÉPINE (*Compt. rend.*, 1924, **179**, 175—178).—A discussion on the probable reactions occurring when pinene under the influence of acids—in particular of hydrochloric acid—is converted into esters of borneol, *iso*borneol, and fenchol, and also into camphene and limonene. F. G. M.

Essential Oils. SCHIMMEL U. CO. (*Report Schimmel u. Co.*, 1923, 1—240; from *Chem. Zentr.*, 1924, i, 2213—2215).—The following data are given for essential oils: essential oil from *Abies pindrow*, d^{15} 0·8655; α_D −10° 41′; n_D^{20} 1·47220; saponification number, *S.N.*, 0; esterification number, *E.N.*, 8·4; Brazilian rosewood oil, d^{15} 0·9120; α_D +6° 20′; n_D^{20} 1·47975; *S.N.*, 0; *E.N.*, 0; acetyl number, 131·6; American *Artemisia* oil, d^{15} 0·9575; α_D −0° 26′; n_D^{20} 1·47750; *S.N.*, 0·6; *E.N.*, 11·2; essential oil from *Nepeta cataria*, var. *citriodora*, Beck, d^{15} 0·8915; α_D −1° 34′; n_D^{20} 1·47485; *S.N.*, 5·6; *E.N.*, 8·4. G. W. R.

Constituents of Resins. X. Pinoresinol and the Natural Resin of Pine. A. ZINKE, A. ERBEN, and F. JELE (*Monatsh.*, 1924, **44**, 371—377).—The crystalline dibenzoate of pinoresinol, $C_{33}H_{28}O_8$, m. p. 159°, is more serviceable for the purification of the α-resin than Bamberger's process of crystallising the potassium salt. On hydrolysis with 10% alcoholic potassium hydroxide the pinoresinol is obtained, m. p. 120—121°. Oxidation of dibenzoylpinoresinol with chromic acid in acetic acid gives two new products, *A* and *B*, benzoic acid also being isolated. The yellow *substance* (*A*),

$C_{32}H_{24}O_{10}$, m. p. 219°, is evidently formed from the original resin by simultaneous loss of a methyl and formation of a carboxyl group. It gives an intense red solution in sodium hydroxide, and when it is heated benzoic acid is formed and a small quantity of oil distils, possessing a eugenol-like odour. The *substance B*, m. p. 148°, has the composition, $C_{20}H_{18}O_5$, and is also soluble in sodium hydroxide. It yields a *bromo* derivative, $C_{20}H_{17}O_5Br$, m. p. 155°. Pinoresinol gives a *di*-p-*bromobenzoate*, m. p. 231—232°, which on oxidation similarly yields two *products*, yellow plates, m. p. 245°, of the composition $C_{32}H_{22}O_{10}Br_2$, corresponding with product *A*, and reddish crystals, m. p. 169—171°, which contain halogen and are insoluble in sodium hydroxide. The structure of pinoresinol is discussed and a partial solution of the problem suggested. R. B.

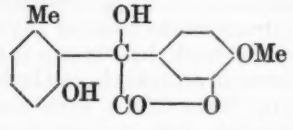
Constitution of Colchicine. A. Windaus (*Annalen*, 1924, **439**, 59—75).—The constitution of colchicine is deduced from its various decomposition products to be best represented by the annexed formula. Treated with concentrated hydrochloric acid, 1 mol. of acetic acid is split off yielding trimethylcolchicinic acid, which on heating with hydrogen iodide loses 3 mols. of methyl iodide and hence contains three methoxyl groups. With benzenesulphonyl chloride this acid yields a dibenzenesulphonyl derivative, existing in two isomeric forms, which on careful hydrolysis give the same *N*-benzenesulphonyltrimethylcolchicinic acid. This behaviour is explained by the presence of a hydroxymethylene group. When warmed for a short time with dilute hydrochloric acid, colchicine loses 1 mol. of methyl alcohol, yielding colchiceine, which, treated with a strongly alkaline solution of potassium iodide, yields a phenol, iodo-*N*-acetylcolchinol, $C_2H_{22}O_5NI$, by the replacement of a –CHO group by iodine, a reaction typical of aromatic hydroxymethylene or hydroxyaldehyde compounds. The presence of a methylene group is shown by the oxidation of colchicine with chromic anhydride to the ketone oxycolchicine; *semicarbazide*, m. p. 220—223°. Oxidation of colchicine, colchiceine, trimethylcolchicinic acid, or iodo-*N*-acetylcolchinol with potassium permanganate yields 3 : 4 : 5-trimethoxy-*o*-phthalic acid, whilst complete oxidation yields oxalic and succinic acids. Oxidation with hot potassium permanganate of the methyl ether of iodo-*N*-acetylcolchinol splits two of the six-membered rings, giving 5(?)-iodo-4-methoxy-*o*-phthalic acid. Reduction of the methyl ether with zinc dust gives *N*-acetylcolchinol methyl ether, which on energetic oxidation with chromic anhydride yields 4-methoxy-*o*-phthalimide, and hence the nitrogen atom is attached to the carbon atom next to the junction with the third ring. The methyl ether therefore contains three different six-membered rings, and since there are fifteen carbon atoms directly combined, it must be a derivative of methylanthracene or methylphenanthrene. *N*-Acetylcolchinol methyl ether, on treatment with methyl-alcoholic



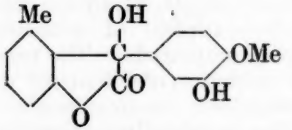
hydrochloric acid, yields colchinol methyl ether, which with 1 mol. of methyl iodide yields the *hydriodide* of *N-methylcolchinol methyl ether*, m. p. 244—245° (decomp.) (*picrate*, m. p. 200°), which with more methyl iodide yields the *hydriodide* of the *tertiary base*, m. p. 236° (decomp.) (*picrate*, m. p. 195—196°), and a *quaternary ammonium salt*, m. p. 231—232° (*picrate*, m. p. 193°), from which by means of silver oxide the *quaternary ammonium hydroxide* is obtained. This on heating in high vacuum yields trimethylamine, water, and 2 : 3 : 4 : 7-*tetramethoxy*-9-*methylphenanthrene*, m. p. 111°, which with hydrogen iodide yields the corresponding tetrahydric phenol, converted on distillation with zinc dust into 9-*methylphenanthrene*, m. p. 88—89°, identified by comparison with a specimen obtained by a rational synthesis. Colchicine is the methyl ether of colchiceine, which is the *N*-acetyl derivative of trimethylcolchicinic acid. Confirmation of these formulæ is obtained by catalytic reduction of colchicine and colchiceine. Each takes up 8 atoms of hydrogen, yielding *octahydrocolchicine*, m. p. 125—126°, and *octahydrocolchiceine*, m. p. 198—200°; *acetyl* derivative, m. p. 160—161°. Oxycolchicine similarly yields *octahydro-oxycolchicine*, m. p. 267—268°. J. W. B.

Phyllodulcin, a Sweet Principle of the Leaves of *Hydrangea Thunbergii*. S. H. Maniwa (*J. Pharm. Soc. Japan*, 1924, No. 507, 348—398; cf. *ibid.*, 1915, No. 406, 1399).—By extracting the leaves of the plant with alcohol three isomerides are obtained: *d*-phyllodulcin, m. p. 120°, $[\alpha]_D$+67° to 69°; *d-iso*phyllodulcin, m. p. 131°, $[\alpha]_D$+20°; and *dl-iso*phyllodulcin, m. p. 131—132°. They contain one methoxy group, two hydroxy groups, and a lactone ring. By fusion with potassium hydroxide, phyllodulcin gives 3 : 4-dihydroxybenzoic acid and 3-hydroxy-*o*-toluic acid, $OH{\cdot}C_6H_3Me{\cdot}CO_2H$. The constitutions of phyllodulcin and *iso*phyllodulcin have been suggested by Asahina and Ueno (*ibid.*, 1916, No. 408, 146) to be (I) or (II):

(I.)



(II.)



The author has synthesised 3-hydroxy-*o*-toluic acid from aceto-*o*-toluidide and identified it with one of the decomposition products of phyllodulcin. Aceto-*o*-toluidide is nitrated to 3-nitro-*o*-toluidine, which is converted successively into a nitrile and an acid amide. By nitrous acid the amide is changed into 3-nitro-*o*-toluic acid, which is reduced, diazotised, and converted into 3-hydroxy-*o*-toluic acid, m. p. 168°. 3-*Methoxy*-o-*toluic acid* has m. p. 137—138° and the *ethoxy* compound, m. p. 126—127° (cf. Asahina and Kondo, *ibid.*, 1922, No. 482, 264). By heating *d*-phyllodulcin with potassium hydroxide, methyl iodide, and methyl alcohol in a sealed tube, d-*phyllodulcin dimethyl ether*, m. p. 87°, is produced. Its lactone ring is opened by heating with alcoholic potassium hydroxide, but is closed again by making the solution acidic. After opening

the lactone ring of the dimethyl ether, it is oxidised with potassium permanganate in the presence of magnesium sulphate, 3-methoxy-*o*-toluic acid being produced. d-*Phyllodulcin diethyl ether* has m. p. 96—97°. By the same method, dl-iso*phyllodulcin dimethyl ether*, m. p. 117°, and *diethyl ether*, m. p. 119—120°, give 3 : 4-dimethoxybenzoic acid and 3-ethoxy-4-methoxybenzoic acid, m. p. 166—167°, respectively. The last is prepared from 5-nitroguaiacol ethyl ether through the amino and cyano compounds. From these results, the constitutions of phyllodulcin and its isomeride are determined to be (I) and (II) respectively. The preparation of *iso*vanillic acid from anethole was attempted. 3-Nitroanisic acid, obtained from anethole by oxidising with nitric acid, is reduced to the amino compound with tin and hydrochloric acid. The hydrolysis of the diazo compound is accomplished with a concentrated sulphuric acid solution of cupric sulphate (D.R.-P. 167211), crystals, m. p. 213—214°, being produced, identical with 3 : 5-dihydroxy-4-methoxybenzoic acid (methyl ester, m. p. 95°) prepared from anisaldehyde. K. K.

Saponins. I. The Sapogenin of the White Soapwort (*Gypsophila sapogenin*). P. Karrer, W. Fioroni, R. Widmer, and H. Lier (*Helv. Chim. Acta*, 1924, **7**, 781—789; cf. Rosenthaler and Ström, A., 1912, i, 640).—The aqueous extract from *Radix saponaria levantica* was concentrated, heated with alcohol and sulphuric acid at 150°, and the sapogenin, termed by the authors *albsapogenin*, extracted with ether. Rosenthaler's formula, $C_{24}H_{34}O_5$ (*loc. cit.*), is rejected in favour of $C_{28}H_{44}O_4$. It yields a *methyl* ester, m. p. 192°, having begun to decompose at about 140°; an *oxime*, m. p. 264—265° (decomp.); a *semicarbazone*, m. p. 272° (cf. Rosenthaler, *loc. cit.*); and an *acetyl* derivative, sintering at 178° and melting at 192—194°. Albsapogenin may thus be formulated $C_{27}H_{42}O(OH)\cdot CO_2H$. When it is reduced by hydrogen and platinum black it yields (the ketonic group having been reduced) the dihydroxycarboxylic acid, albsapogenol, m. p. 321—322°; the *diacetyl* derivative sinters at 150°, m. p. 169°. Albsapogenin is oxidised by a cold mixture of chromic and acetic acids to *albsapogenic acid*, $C_{26}H_{41}O\cdot CO_2H$, m. p. 256°. When albsapogenin is heated with 80% sulphuric acid at 100—120° only 1 mol. of carbon monoxide is evolved, proving that it is an α-ketocarboxylic acid. When it is boiled with hydrochloric and acetic acids, or with sulphuric and acetic acids (although here another action takes place), but not with acetic acid alone, it is converted into *albsapin*, which is not an acid, but possibly a lactone. W. A. S.

Decomposition of Chlorophyllic Extracts. A. Mailhe (*Compt. rend.*, 1924, **178**, 1988—1990).—The alcoholic extract of plants after evaporation of the solvent ("chlorophyllic extract") was submitted to the action of anhydrous zinc chloride and magnesium chloride at various temperatures. Distillation with the latter substance at 300° yields a gas of the composition: carbon dioxide 57%, carbon monoxide 14%, hydrogen 20·5%, ethylenic hydrocarbons 9%. Simultaneously, a slightly acid liquid is obtained

consisting of paraffins and ethylenic hydrocarbons. This was fractionated and from the fractions of higher boiling point, crystals of dinonyl ketone were deposited. The acidity of the distillate is due to partial hydrolysis of the catalyst. H. J. E.

Hydrolytic Product of Chlorophyll containing Iron. S. MATYSIAK (D.R.-P. 376287; from *Chem. Zentr.*, 1924, i, 968).—Phæophytin free from magnesium, obtained by the hydrolysis of chlorophyll, is treated with ferric acetate. An amorphous, dark red *substance* is obtained which shows a biological similarity to hæmoglobin. It contains 2·53% of iron, and chars at 263° after sintering at 250°. G. W. R.

Bile Pigments. VIII. Mesobiliviolin, Mesobiliviolinogen, and the Condensation of Mesobilirubinogen with Aldehydes. Bisazo Pigment from Mesobilirubin. H. FISCHER and G. NIEMANN (*Z. physiol. Chem.*, 1924, **137**, 293—316).—Mesobilirubin, m. p. 295—315°, is prepared by heating bilirubin with potassium methoxide and hydrazine in a closed tube at 180°. In alkaline solution, it is converted by atmospheric oxidation into mesobiliverdin and with ammoniacal copper solution it gives a crystalline *copper* salt. Mesobilirubin reacts with diazobenzenesulphonic acid, giving a violet pigment. On coupling it with diazobenzene chloride, a violet *pigment*, $C_{45}H_{48}O_6N_8,2HCl$, m. p. 192° (decomp.), is obtained. The methyl ester yields a similar bluish-grey *pigment*, $C_{47}H_{52}O_6N_8,2HCl$, m. p. 178° (decomp.). Mesobilirubinogen (A., 1911, i, 1005) gives a double *salt*, $C_{33}H_{44}O_6N_4,2FeCl_3$, when treated with ferric chloride and hydrochloric acid. *Mesobiliviolin*, $C_{33}H_{40}O_8N_4$, m. p. 215° (decomp.), is obtained by heating a suspension of this double salt in 4% hydrochloric acid on a water-bath; it separates in violet globules. With alcoholic zinc acetate, it shows a fluorescence characteristic of urobilin. On hydrogenation in alcoholic solution in presence of platinum, it yields *mesobiliviolinogen*, $C_{33}H_{48}O_5N_4$, fine prisms, m. p. 228—230°. In its properties it resembles mesobilirubinogen, giving an intense aldehyde reaction, but with zinc acetate it shows urobilin fluorescence only after some time. Mesobilirubinogen condenses with benzaldehyde in presence of hydrochloric acid giving a yellow monobasic *acid* (benzylidenebilirubic acid), $C_{24}H_{28}O_3N_2$, m. p. 240°. Its methyl ester, $C_{25}H_{30}O_3N_2$, m. p. 212—213°, is similar to, although not identical with, xanthobilirubin ester. On oxidation with concentrated nitric or chromic acid, the monobasic acid yields methylethylmaleinimide and benzoic acid, respectively. With *p*-nitrobenzaldehyde, mesobilirubinogen yields a similar condensation *product* (*p-nitrobenzylidenebilirubic* acid), $C_{24}H_{27}O_5N_3$, m. p. 253°. D. R. N.

Action of Oxalyl Chloride on Naphthols. M. GIUA and V. DE FRANCISCIS (*Gazzetta*, 1924, **54**, 509—516).—4 : 5-Benzocoumaran-2 : 3-dione (cf. A., 1917, i, 204) may be obtained in good yield by heating on the water-bath a carbon disulphide solution of β-naphthol (1 mol.) and oxalyl chloride (1 mol.), and, when the evolution of hydrogen chloride tends to moderate, adding a small

quantity of aluminium chloride. When this compound, suspended in alcohol, is treated with an organic base (1 mol.), the reddish-yellow diketone passes slowly into solution, giving a colourless or pale yellow liquid and sometimes a white precipitate, which is probably the substituted amide of the naphtholglyoxylic acid, formed by opening of the lactonic ring. When the action of the base and of heat is continued, the ring becomes closed again, with elimination of a molecule of water or alcohol and condensation of the amino group and a ketonic group : $C_{10}H_6<^{CO}_{O}>CO+NH_2X \longrightarrow$

$$C_{10}H_6<^{CO\cdot CO\cdot NHX}_{OH} \longrightarrow C_{10}H_6<^{CO}_{O}>C{:}NX.$$

4 : 5-*Benzocoumaran*-2 : 3-*dioneanil*, $C_{10}H_6<^{CO}_{O}>C{:}NPh$, obtained by the action of aniline on the diketone, forms yellow needles, m. p. 126—127° (slight decomp.), and gives an intense, deep red coloration with concentrated sulphuric acid. The *o-methylanil*, $C_{19}H_{13}O_2N$, prepared by means of *o*-toluidine, has m. p. 166—167°.

4 : 5-*Benzocoumarophenazine*, $C_{10}H_6<^{C{:}N}_{O\cdot C{:}N}>C_6H_4$, prepared by the action of *o*-phenylenediamine on 4 : 5-benzocoumaran-2 : 3-dione, forms orange-yellow needles, m. p. 286—287°.

4 : 5-Benzocoumaran-2 : 3-dione forms a *picrate*, $C_{18}H_9O_{10}N_3$, m. p. 109°; a *monosemicarbazone*, $C_{13}H_9O_3N_3$, m. p. 240—241°; and a *monophenylhydrazone*, $C_{18}H_{12}O_2N_2$, m. p. 226—227°.

Ethyl 2 : 1-*naphtholglyoxylate phenylosazone*,

$$OH\cdot C_{10}H_6\cdot C(:N_2HPh)\cdot C(:N_2HPh)\cdot OEt,$$

obtained by the action of phenylhydrazine (2 mols.) on 4 : 5-benzocoumaran-2 : 3-dione, forms white needles ($+C_6H_6$), m. p. (rapid heating) 165—166° (slight decomp.).

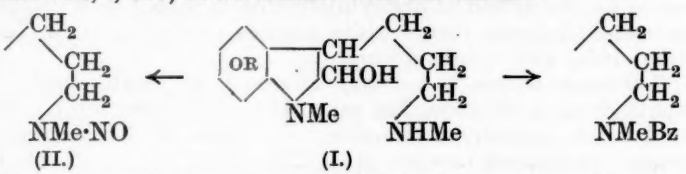
6 : 7-*Benzocoumaran*-2 : 3-*dione*, obtained in small yield from α-naphthyloxalyl chloride, has m. p. 146—147° (decomp.). When treated with *o*-phenylenediamine, it yields 6 : 7-*benzocoumarophenazine*, garnet-red needles, m. p. 232—233°. T. H. P.

Colouring Matter of the Blue Pansy [" Emperor William "]. G. S. Currey (*Proc. Roy. Soc.*, 1924, **B**, **96**, 374—382).—The petals of the blue pansy, " Emperor William," are shown to contain violanin (6·3%, as potassium salt, of dried petals). The pigment (crystalline chloride) was deep ruby-red, as stated by Everest (A., 1918, i, 420). Rutin (9·68%) was also isolated, but as the presence of myricetin or cyanidin was not detected, no further evidence is obtained that an anthocyan pigment is formed within a flower by reduction of the corresponding flavonol pigment (cf. Everest and Hall, A., 1921, i, 485). A. J. H.

Degradation of Hydrogenated Derivatives of Eserine. M. and M. Polonovski (*Compt. rend.*, 1924, **179**, 178—181; cf. A., 1923, i, 700, 831, 939, 940).—Hydroetheserolene, prepared by the reduction of etheserolene either with zinc and hydrochloric acid or with colloidal palladium or platinum in neutral or acid solution, has now been purified by conversion into the *hydrochloride*,

$C_{14}H_{19}ON,HCl$, m. p. 177°. The regenerated pure base has $[\alpha]_D$ +3° in 95% alcohol, and +35° in light petroleum, but undergoes inversion in acids, having $[\alpha]_D$ −31° in dilute hydrochloric acid. *Hydroeseretholmethine methiodide*, m. p. 140° (zinc chloride *additive* compound, m. p. 263°), when warmed in concentrated solution with sodium hydroxide undergoes two simultaneous changes, losing methyl iodide to give hydroeseretholmethine, and losing trimethylamine hydriodide to give hydroetheserolene (*chlorozincate*, m. p. 248°). It is concluded that reduction of etheserolene to hydroetheserolene does not involve the saturation of an ethylenic linking present in the former, and two possible constitutional formulæ for each of the two bases are suggested. F. G. M.

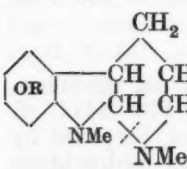
Nitroso and Benzoyl Derivatives of Eserine. M. and M. Polonovski (*Compt. rend.*, 1924, **179**, 334—336; cf. A., 1923, i, 831).—Eserine and eserethole can react as secondary bases in the formation of nitroso and benzoyl derivatives. By the addition of a concentrated solution of sodium nitrite to eserine dissolved in a slight excess of acetic acid, *nitrosoeserine* (II) is obtained as a yellow, neutral oil. Similarly, eserethole yields *nitrosoeserethole*, a viscous, neutral, optically inactive oil, soluble in dilute acids, but which forms no crystalline salts except the *picrate*, m. p. 133—134°. By the Schotten-Baumann reaction on eserethole suspended in dilute sodium hydroxide, *benzoyleserethole* is obtained as a viscous mass which is pulverisable in the presence of ether and petroleum, ($[\alpha]_D$ −51°). The formation of these derivatives can only be explained on the open-chain formula for eserine ("eserinol," I) (cf. this vol., i, 980) in accordance with the scheme :



(II.) (I.)

When an eserine salt is decomposed in aqueous solution by sodium hydrogen carbonate, an eserine *hydrate*, $C_{15}H_{21}O_2N_3,H_2O$, m. p. 82°, is obtained. This compound, however, is not regarded as having the eserinol structure. J. W. B.

Hydrogen Derivatives of Eserine. M. and M. Polonovski (*Compt. rend.*, 1924, **178**, 2078—2081).—A correction to previous work (A., 1923, i, 831). The formula previously suggested for eserine (quoted with an obvious misprint) with an ethylenic linking in the pyrrole nucleus is untenable, principally because the quaternary salts can combine with but 1 mol. of hydrogen, giving a completely saturated open-chain methine base, although other evidence also is adduced. The new formula suggested is appended. Reduction in acid solution is then explicable only on the assumption that the ring is opened, at the point indicated by the dotted line, as in the



case of the reduction of the quaternary salts. This view is supported by a reaction with methyl iodide towards which hydroeserethole behaves as a secondary open-chain base. L. J. H.

Quebrachamine. (Miss) E. Field (*J. Chem. Soc.*, 1924, **125**, 1444—1450).—This alkaloid, now being prepared commercially from quebracho bark (presumably as a by-product in the manufacture of aspidospermine), has been investigated in the hope of discovering some relationship between it and quebrachine and aspidospermine (from the same bark). Cow (*J. Pharm. Exp. Ther.*, 1913—1914, **5**, 341) has found their physiological actions to be similar and to differ only in intensity. Quebrachamine, $C_{19}H_{26}N_2$, has m. p. 147° (cf. Hesse, A., 1882, 742), $[\alpha]_D$ −109·5° in acetone, and distils without appreciable decomposition under high vacuum at 240—250°. It is feebly basic and forms a *sulphate*, $C_{19}H_{26}N_2,H_2SO_4,2H_2O$, sparingly soluble in cold water; the *oxalate* has m. p. 217°. The base appears to be fully saturated, and does not absorb hydrogen in the presence of colloidal platinum. It is apparently a monoacidic tertiary base; the *methiodide* has m. p. 234°, the *methosulphate* m. p. 235°. The nature of the second nitrogen atom has not been definitely ascertained; attempts to methylate it resulted in tarry products. Its behaviour towards nitrous acid suggests that it may be in the form of an imino group. On adding a solution of sodium nitrite to quebrachamine in acetic acid, a green oil is precipitated, changing to a yellow, amorphous solid. Attempts to form phenylcarbimido and acetyl derivatives were unsuccessful. The colour reactions of quebrachamine suggest that it contains an indole grouping. Quebrachamine *picrate*, m. p. 195—196°, exhibits chromoisomerism.

These properties are in harmony with the presence of a non-basic imino group and a benzene ring. The existence of the latter is indicated by the formation of picric acid when the alkaloid is heated with 30% nitric acid at 150°. Other oxidising agents react readily, but the products are amorphous mixtures. Bromine reacts with quebrachamine to form an unstable *perbromide*, $C_{19}H_{24}N_2Br_6$, m. p. 160° (decomp.), which, on prolonged boiling with water, loses bromine to give a *bromo* compound, $C_{19}H_{23}ON_2Br_3$, not melting at 290°. The compound is not changed by sodium hydroxide, and hence is not a hydrobromide. On boiling with sodium in alcoholic solution, quebrachamine is regenerated.

The high hydrogen content of the alkaloid precludes the presence of more than one benzene ring. A striking resemblance between the molecular formulæ of quebrachamine and aspidospermine ($C_{22}H_{30}O_2N_2$) is pointed out. Hydrolysis of the latter (cf. Ewins, T., 1914, **105**, 2738) causes the removal of a methoxyl and a *N*-acetyl group and leaves a base, aspidosine, $C_{19}H_{26}ON_2$, a phenolic substance, of which the parent substance, $C_{19}H_{26}N_2$, has the same empirical formula as quebrachamine. Aspidosine, like quebrachamine, is a monoacidic tertiary base and contains an imino group and a benzene ring. On the other hand, quebrachamine cannot be acetylated, and forms only a monomethiodide, whilst both

nitrogen atoms in deacetylaspidospermine undergo methylation. Further, aspidospermine and its derivatives do not give the reactions of indoles. Attempts to remove the hydroxyl group from aspidosine were unsuccessful. No similar relationship between quebrachamine and quebrachine (yohimbine) is apparent, and reasons are given to show they can not have the same skeleton. A. C.

Spectrographic Study of Vegetable Alkaloids. Absorption of Ultra-violet Rays by Alkaloids of the *iso*Quinoline and Morphine Groups. P. STEINER (*Bull. Soc. Chim. biol.*, 1924, **6**, 231).—A detailed study of the ultra-violet absorption spectra of the principal *iso*quinoline and morphine alkaloids and of the compounds from which they are derived. The results of earlier work on the absorption spectra of some of these alkaloids is in general confirmed and a large amount of new quantitative data is presented.

Each alkaloid examined has a definitely characteristic ultra-violet absorption spectrum, which is closely related to that of the principal aromatic nucleus in the molecule when that nucleus is comparatively little modified (*e.g.*, the *iso*quinoline nucleus in papaverine). On the other hand, when the principal nucleus is much modified, the spectrum of the alkaloid is quite unlike that of the nucleus (*e.g.*, *iso*quinoline and berberine). When the molecule is made up of two large aromatic nuclei, its spectrum is determined almost entirely by one of them.

The author has specially investigated cotarnine and hydrastinine with a view to decide between the three structural formulæ which have been proposed for these substances. The absorption curves provide strong evidence that cotarnine has the ·CH(OH)·NMe· structure in hexane and ether solutions, thus confirming the conclusions of Dobbie, Lauder, and Tinkler (cf. T., 1903, **83**, 598), and that it has the ·CH:NMe(OH)· structure in aqueous and acid solutions; in alcoholic solution it is apparently a mixture of these two types. There is no evidence for the aldehydic formula.

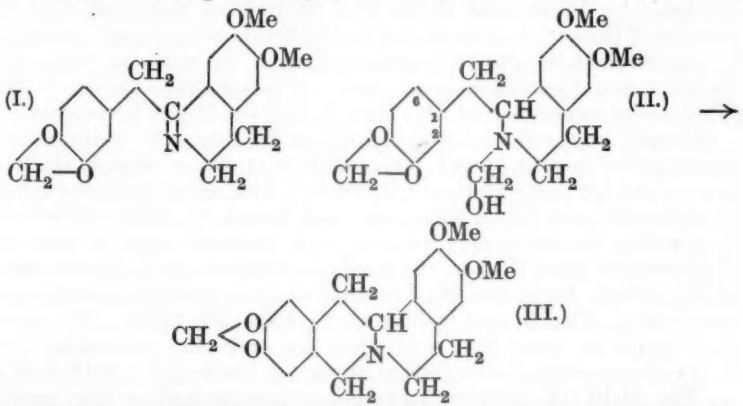
The alkaloids can be identified and determined by means of their absorption spectra, but the method has been worked out only for solutions of the pure substances. C. T. G.

Preparation of a Mercury Quinine Compound. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (Swiss Pat. 100410; from *Chem. Zentr.*, 1924, i, 2206).—A solution obtained by shaking a suspension of mercuric oxide with quinine sulphate solution is added to ethyl alcohol, whereby a precipitate of *mercuriated quinine disulphate* is obtained. G. W. R.

***ψ-epi*Berberine.** J. S. BUCK and W. H. PERKIN, jun. (*J. Chem. Soc.*, 1924, **125**, 1675—1686).—As *epi*berberine has hitherto been obtained only from cryptopine (**T.**, 1918, **113**, 492), its synthesis was attempted by a method resembling that for berberine (cf. Pictet and Gams, A., 1911, i, 807), and 1-*homopiperonyl*-6 : 7-*dimethoxytetrahydro*isoquinoline was obtained, but the alkaloid produced from it by the action of formaldehyde and hydrochloric acid was shown to be *tetrahydro*-ψ-epi*berberine*, instead of tetrahydro*epi*berberine.

For preparation of the starting materials, veratraldehyde from vanillin was condensed with ethyl acetate in presence of sodium to 3 : 4-dimethoxycinnamic acid, which was reduced by sodium amalgam to 3 : 4-dimethoxyphenylpropionic acid (cf. Perkin and Robinson, T., 1907, **91**, 1079). The acid was converted by dry ammonia at 220—230° into its *amide*, m. p. 121°, which with sodium hypochlorite gave a 70% yield of homoveratrylamine (cf. Decker, A., 1913, i, 272). Condensation of piperonal with hippuric acid gave the azlactone, which was hydrolysed to benzoic acid and piperonylpyruvic acid (Kropp and Decker, A., 1909, i, 248), and oxidation of the latter with hydrogen peroxide (cf. Mauthner, A., 1910, i, 115) yielded homopiperonylic acid.

Homopiperonoylhomoveratrylamine, $CH_2{:}O_2{:}C_6H_3{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_3(OMe)_2$, needles, m. p. 130—131°, was prepared (*a*) by heating homopiperonylic acid with homoveratrylamine at 180—200°, or (*b*) by addition of homopiperonyl chloride (prepared by use of thionyl chloride) to homoveratrylamine in presence of potassium hydroxide. Digestion with phosphorus oxychloride in boiling toluene gave a phosphate, from which alkali liberated 1-*homopiperonyl*-6 : 7-*dimethoxy*-3 : 4-*dihydro*isoquinoline (yield 80%) (I.) It is a strong base (colourless *hydrochloride*, m. p. 200°; *picrate*, m. p. 197°); except when pure and dry, it is oxidised by air to a *base*, $C_{19}H_{17}O_5N$, m. p. 152°. Reduction with sulphuric acid and zinc forms 1-*homopiperonyl*-6 : 7-*dimethoxytetrahydro*isoquinoline, irregular plates, m. p. 96° (a strong base, forming colourless *hydrochloride* and *sulphate*). Condensation of this substance with methylal was unsuccessful (cf. Pictet and Gams, *loc. cit.*), but its methyl-alcoholic solution was condensed with formaldehyde in presence of sodium hydrogen carbonate and the product (II) was treated with hot concentrated

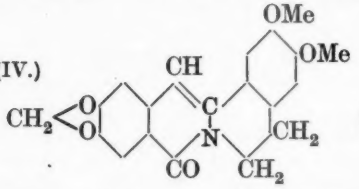


hydrochloric acid. The *hydrochloride* of *tetrahydro-ψ-epiberberine* was isolated and was decomposed with potassium carbonate, giving the *base*, jagged prismatic needles, m. p. 160—161° (III). It is distinguished from tetrahydro*epi*berberine by the m. p. and by the mixed m. p. The *picrate* melts at 149—150° (decomp.).

No trace of tetrahydro*epi*berberine was formed, showing that ring formation (II → III) takes place solely with the hydrogen atom in position 6, and not with that in position 2.

Tetrahydro-*ψ-epi*berberine was oxidised by iodine in alcoholic solution, in presence of sodium acetate, and the resulting periodide was decomposed with sulphurous acid, yielding *ψ*-epi*berberinium iodide*, $C_{20}H_{18}O_4NI$, yellow, rhombic prisms, m. p. about 303°. Digestion of the iodide with silver chloride gave *ψ*-epi*berberinium chloride*, yellow, existing in 3 modifications: $C_{20}H_{18}O_2NCl,4\frac{1}{2}H_2O$, $C_{20}H_{18}O_4NCl,2\frac{1}{2}H_2O$, and the dimorphous anhydrous salt. The *chloroplatinate* and dimorphous *picrate*, m. p. 105°, were obtained. Decomposition of the chloride with potassium hydroxide is exactly analogous to the decomposition of *epi*berberinium chloride (T., 1918, **113**, 517). The products are (*a*) *oxy-ψ*-epi*berberine* (IV), almost colourless, m. p. 206°, differing from oxy*epi*berberine by its m. p., and (*b*) *dihydro-ψ*-epi*berberine* (V), yellow, rhombic prisms, m. p. 173°, distinguished from dihydro*epi*berberine by their mixed

(IV.)



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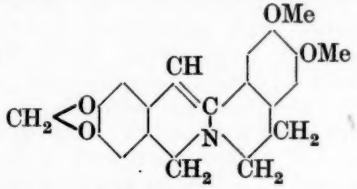

m. p. It forms pale yellow salts; *hydrochloride*, m. p. 266°; *hydriodide*, m. p. about 281°, with blackening. F. M. H.

ψ-Berberine. R. D. Haworth, W. H. Perkin, jun., and J. Rankin (*J. Chem. Soc.*, 1924, **125**, 1686—1701).—Repetition of a synthesis by Pictet and Gams (A., 1911, i, 807) showed that the product of the action of methylal and hydrochloric acid on 1-veratryl-6 : 7-methylenedioxytetrahydro*iso*quinoline is not, as they concluded, tetrahydroberberine, but *tetrahydro-ψ-berberine*. Their synthesis of oxyberberine (A., 1911, i, 483) could not be repeated.

Starting materials were prepared as follows: 3 : 4-dimethoxyphenylpyruvic acid, yield 50%, obtained by a modification of Kropp and Decker's method (A., 1909, i, 248), gave 3 : 4-dimethoxyphenylacetic acid (Cain, Simonsen, and Smith, T., 1913, **103**, 1036). A pyridine solution of piperonal and malonic acid in presence of piperidine gave 3 : 4-methylenedioxycinnamic acid (quantitative yield), which furnished 3 : 4-methylenedioxyphenylpropionic acid (yield 85%) (Perkin and Robinson, T., 1907, **91**, 1079). The *amide* was prepared from the acid chloride and was converted into 3 : 4-methylenedioxyphenylethylamine (cf. Decker, A., 1913, i, 272).

The yield of homoveratroylhomopiperonylamine was greatly improved; it was obtained (*a*) by condensation of 3 : 4-dimethoxyphenylacetyl chloride with 3 : 4-methylenedioxyphenylethylamine, or (*b*) by heating this amine with 3 : 4-dimethoxyphenylacetic acid at 180°. By boiling a toluene solution of homoveratroylhomopiperonylamine with phosphorus oxychloride, the yield (75%) of

1-*veratryl*-6 : 7-*methylenedioxydihydroisoquinoline* is much higher than when phosphoric oxide is used. Pictet and Gams (*loc. cit.*) describe the base as amorphous, m. p. 68—70°, salts indefinite. It is now found to be crystalline, m. p. 88° (*hydrochloride*, m. p. 62°, loses water of crystallisation and then melts at 125°; *hydriodide*, m. p. 239—240°; *picrate*, m. p. 206°). In air, it tends to oxidise to a *base*, $C_{19}H_{17}O_5N$, m. p. 151°. Reduction of the dihydro*iso*quinoline by means of tin and hydrochloric acid yielded 1-*veratryl*-6 : 7-*methylenedioxytetrahydroisoquinoline* (I), prisms, m. p. 84° (*hydrochloride*, prisms, m. p. 236°, *sulphate*, plates, m. p. 136—137°, *picrate*, yellow needles, m. p. 185—187°); this is analogous to similar tetrahydro*iso*quinolines, which all melt below 100°, but Pictet and Gams gave as m. p. of the base 208—210° and found the salts difficult to crystallise. When (I) is condensed with

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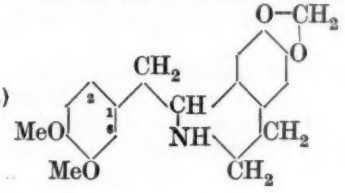

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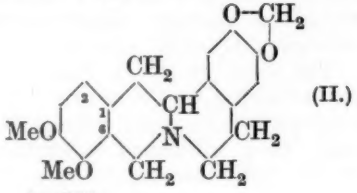

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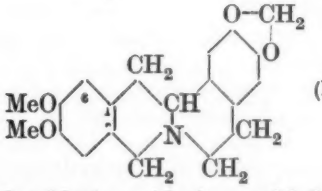


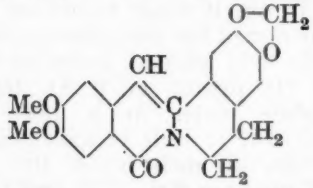
methylal and hydrochloric acid, it would be expected that III would be formed, but Pictet and Gams claim that they obtained *tetrahydroberberine* (II). This is especially anomalous, since condensation of 1-homopiperonyl-6 : 7-dimethoxytetrahydro*iso*quinoline has now been shown to occur normally (cf. Buck and Perkin, this vol., i, 1096). When 1-veratryl-6 : 7-methylenedioxytetrahydro*iso*quinoline was treated exactly as in the original synthesis, it gave a *base*, $C_{20}H_{21}O_4N$, small needles, m. p. 177°: but tetrahydroberberine melts at 169° and the mixture at 142—144°. Therefore this must be isomeric with tetrahydroberberine (II) and has been named *tetrahydro-ψ-berberine* (III) (*hydrochloride* darkens at 222°, m. p. 228—230°; *hydriodide* softens at 178°, m. p. 222°; *sulphate*, m. p. 168°; *picrate*, m. p. 176°; *methiodide*, prismatic needles, m. p. 256° [decomp. 260°]). The yield was small and an amorphous substance was produced containing no tetrahydroberberine. A much better yield (60%) of tetrahydro-ψ-berberine is obtained by condensing a methyl-alcoholic solution of the tetrahydro*iso*quinoline with formaldehyde and decomposing the formyl derivative with hydrochloric acid (cf. Decker, *loc. cit.*).

Tetrahydro-ψ-berberine is oxidised by iodine in alcoholic solution to *ψ-berberinium iodide*, canary-yellow needles, m. p. 274° (decomp.). Silver chloride converts this into *ψ-berberinium chloride*, obtained

anhydrous from alcohol (darkens at 270°, decomp. 300°), from water as $C_{20}H_{18}O_4NCl,4\frac{1}{2}H_2O$ (*picrate*, decomp. 305°, whereas berberinium picrate melts at 239°).

When ψ-berberinium chloride is warmed with aqueous potassium hydroxide, there are obtained *oxy-ψ-berberine* (IV), almost colour-

(IV.)



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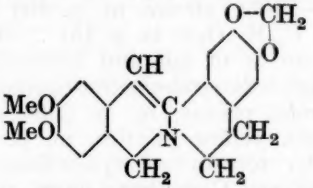
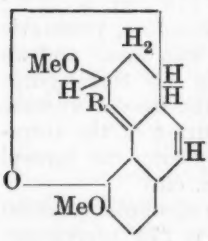


less needles, m. p. 268°, mixed m. p. with oxyberberine, 184—186°, and *dihydro-ψ-berberine* (V), pale yellow needles, m. p. 165—167°, mixed m. p. with dihydroberberine, 141—143°, m. p. of *hydrochloride*, 253—255° (decomp.).

The work by which Pictet and Gams claim to have synthesised oxyberberine was repeated. By condensing the hydrochloride of homopiperonylamine with methylal in presence of hydrochloric acid they obtained methylene-6 : 7-dioxytetrahydro*iso*quinoline (norhydrohydrastinine), as an oil, b. p. 197—199°/50 mm., m. p. of hydrochloride, 255—267°. Repetition now gave the *hydrochloride* (small yield, m. p. 275°), from which the crystalline *base*, m. p. 80—81°, was obtained. Decker and Becker showed that if methylal is replaced by formaldehyde, a good yield of methylenehomopiperonylamine is obtained and can be converted into norhydrohydrastinine (A., 1913, i, 291), so this method was adopted. Pictet and Gams converted crude norhydrohydrastinine into its *o*-nitrobenzoyl derivative, m. p. 104°, but the m. p. of this derivative, as prepared from the pure base, was now found to be 154°. Their next step was to condense it with methyl opianate and decompose with alcoholic potassium hydroxide, when it is stated that oxyberberine was formed. But on repeating the experiment, no trace of it could be isolated; it is moreover shown that when oxyberberine is treated with potassium hydroxide, under the conditions of the experiment of Pictet and Gams, it is completely decomposed to a phenolic substance. F. M. H.

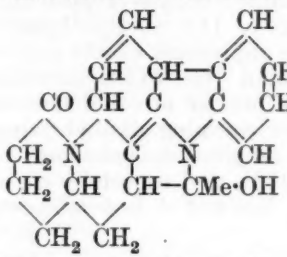
Constitution of Morphine. F. Faltis and A. Suppan (*Pharm. Monatsh.*, 1923, **4**, 189—192; from *Chem. Zentr.*, 1924, i, 918—919).—Hydrogenation of either α- or β-dimethylmorphimethine yields the same product, four hydrogen atoms being absorbed. The two methine bases differ only in the position of the olefinic linkings. The annexed formula is suggested for β-dimethyldimorphimethine; it explains the relationship of the β- and ε-methines. *α-Tetrahydrodimethylmorphine*, $C_{20}H_{29}O_3N$, m. p. 43—46°, is obtained by the catalytic reduction of α-dimethylmorphimethine. *Tetrahydrodimethylmorphimethine chloroaurate* has m. p. 141—143° (decomp.). The



methiodide decomposes at 247°. β-*Dihydrodimethylmorphimethine*, obtained by partial reduction of the β-methine, has m. p. 115°.
G. W. R.

Preparation of an Additive Product of Codeine. O. HINSBERG (D.R.-P. 377588; from *Chem. Zentr.*, 1924, i, 968).—Codeine and *p*-acetaminophenol yield an *additive* compound of composition $C_{18}H_{21}O_3N,OH{\cdot}C_6H_4{\cdot}NHAc$, m. p. 125°. G. W. R.

Constitutional Formula of Strychnine. III. E. OLIVERI-MANDALÀ (*Gazzetta*, 1924, **54**, 516—528).—In the light of present knowledge concerning the reactions of strychnine and *iso*strychnine (cf. A., 1923, i, 702, 1223), the formulæ which best express the structures of these two bases are respectively,



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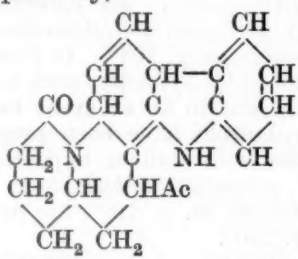
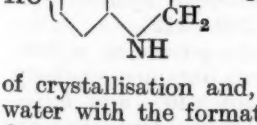


(cf. Perkin and Robinson, T., 1910, **97**, 305). T. H. P.

Preparation of Acyl*apo*cincholoiponitriles. A. KAUFMANN (D.R.-P. 382911; from *Chem. Zentr.*, 1924, i, 1595—1596).—Acylcincholoiponamides are treated with alkali hypohalogenites. *Benzoylcincholoiponamide* (1-*benzoyl*-3-*ethylpiperidinoacetamide*), m. p. 88—89°, is converted by alkaline hypobromite into *benzoyl*apo*cincholoiponitrile* (1-*benzoyl*-3-*ethylpiperidine*-4-*carboxylonitrile*). *Benzoyl*apo*cincholoiponamide* has m. p. 144°.

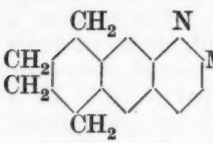
Isolation from Casein of an Amino-acid of the Indole Group with the Composition $C_{11}H_{14}O_3N_2$. E. ABDERHALDEN and H. SICKEL (*Z. physiol. Chem.*, 1924, **138**, 108—117).—The amino-acid previously isolated from casein and regarded as a hydroxytryptophan (Abderhalden and Kempe, A., 1907, i, 808) has been found to have the composition $C_{11}H_{14}O_3N_2,2\frac{1}{2}H_2O$. It has m. p. 146° (slow heating), $[\alpha]_D^{22}$ −28·68°, −28·10° (aqueous solution), and, from its colour reactions, is provisionally considered to be a hydroxydihydrotryptophan of the annexed structure. When dried at 105° in a vacuum over phosphorus pentoxide it loses its water of crystallisation and, at the same time, appears to lose further water with the formation of an anhydride. It forms a *dibenzoyl* derivative, decomposing at 136° after sintering at 72°. E. S.



Chemical Functions of Hypnotics, and of Hydantoin Derivatives in particular. A. LUMIÈRE and F. PERRIN (*Bull. Soc. chim.*, 1924, [iv], **35**, 1022—1026).—The most active hypnotics

known belong to the aliphatic series and contain a quaternary carbon atom linked to alkyl groups. The methyl derivatives are inactive, and the hypnotic effect appears to increase with replacement of methyl by homologous radicals, up to a solubility limit. Of the dialkylhomophthalimides, $CO<\begin{matrix}NH-CO\\ CR_2-C_6H_4\end{matrix}$, obtained by the action of alkyl iodides on homophthalimide, diethylhomophthalimide, *ethylpropylhomophthalimide*, m. p. 117°, and *diallylhomophthalimide*, m. p. 140°, are hypnotic, whilst *dipropylhomophthalimide*, m. p. 128°, is inactive. Similarly, among the dialkylacetylacetamides, obtained by the action of alkyl halides on the amides in the presence of sodium ethoxide, the following order of hypnotic activity holds: acetyldiethylacetamide > *acetyldipropylacetamide*, m. p. 100° > *acetyldiallylacetamide*, m. p. 115° > *acetylethylisobutylacetamide*, m. p. 108°. In view of the unpleasant effects sometimes produced by hypnotics such as "nirvanol" (phenylethylhydantoin) which contain an aromatic radical, a number of other derivatives of hydantoin have been prepared by warming dialkylcyanoacetamides with sodium hypochlorite. *Ethylisobutylhydantoin*, m. p. 199°, *propylisobutylhydantoin*, m. p. 173°, and especially dipropylhydantoin, m. p. 199°, are hypnotic, but not *di*-isobutylhydantoin, m. p. 220°. R. B.

Course of the Quinaldine Synthesis with β-Aminotetrahydronaphthalene. J. Lindner, M. Djulgerowa, and A. Mayr (*Monatsh.*, 1924, **44**, 337—347).—Experiments on the course of the quinaldine synthesis with β-aminotetralin (*ar*-β-tetrahydronaphthylamine) show that both the linear and the angular compound are produced (cf. Braun and Gruber, A., 1922, i, 762), but the proportions could not be determined owing to the difficulty of separation. High concentrations of hydrochloric acid appeared to favour the synthesis, and from the reaction product after adding alkali, distilling in a vacuum, and removing unchanged β-tetrahydronaphthylamine as *benzoyl*-ar-β-*tetrahydronaphthylamine*, m. p. 167°, the two quinaldines are separated by fractional crystallisation of the picrates from water, or extraction of the hydrobromides with benzene or fractional precipitation of the hydrochlorides or hydrobromides in alcoholic solution with ether. 6 : 7-*Tetramethylenequinaldine* (annexed formula), m. p. 45°, obtained finally by decomposition of the picrate with ammonia and extraction with benzene, gives a hygroscopic *hydrochloride*, $C_{14}H_{15}N,HCl$, m. p. 209—212°, a *hydrobromide*, m. p. 212°, and a *picrate*, m. p. 206°.



5 : 6-*Tetramethylenequinaldine*, m. p. 57°, was obtained similarly. The *hydrochloride*, $C_{14}H_{15}N,HCl$, m. p. about 240°, and *hydrobromide*, $C_{14}H_{15}N,HBr$, m. p. 220°, are non-hygroscopic and are less soluble than the isomeric compounds. The *chromate* is orange, but rapidly turns brown. The *picrate*, m. p. 190°, is less soluble in water than the picrate of the isomeric quinaldine, m. p. 170°. The constitution of the base is established by its dehydrogenation

at 700° to β-naphthoquinaldine, m. p. 81·5—82° (cf. Döbner and Miller, A., 1884, 1373).

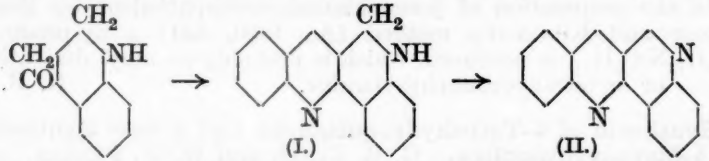
In the preparation of β-aminotetrahydronaphthalene by Bamberger and Kitschelt's method (A., 1890, 631) a by-product, $C_{10}H_{12}N{\cdot}C_5H_{11}$, is produced, which is probably an amyl derivative of *ar-* or *ac*-tetrahydronaphthylamine. R. B.

Synthesis of 4-Tetrahydroquinolone and a new Synthesis of 4-Methoxyquinoline. G. R. Clemo and W. H. Perkin, jun. (*J. Chem. Soc.*, 1924, **125**, 1608—1622).—Condensation, in presence of alkali, of toluene-*p*-sulphonanilide and β-chloropropionic acid yielded *toluene*-p-*sulphonyl*-β-*anilinopropionic acid*, m. p. 144° (*methyl* ester, m. p. 61—62°). The yield of a *by-product*, $2C_{16}H_{17}O_4NS,H_2O$ (?), m. p. 213°, can be increased by varying the conditions. Toluene-*p*-sulphonyl-β-anilinopropionic acid was converted by phosphoric oxide in boiling xylene into *toluene*-p-*sulphonyl*-4-*tetrahydroquinolone*, m. p. 140—141°. Hydrolysis with hydrochloric acid liberated 4-*tetrahydroquinolone*, $C_6H_4<\begin{matrix}CO\text{-}CH_2\\ NH\cdot CH_2\end{matrix}$, b. p. 195°/20 mm., m. p. 144°.

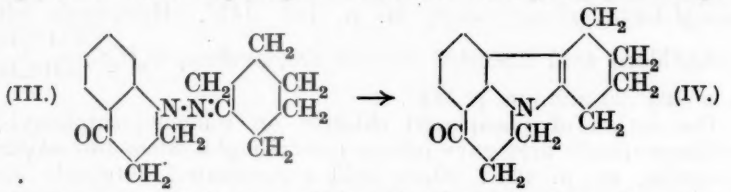
The action of phosphoryl chloride on toluene-*p*-sulphonyl-β-anilinopropionic acid gave *toluene*-p-*sulphonyl*-3-*chloro*-4-*tetrahydroquinolone*, m. p. 124°. Since cold concentrated sulphuric acid eliminates hydrogen chloride, the chlorine atom cannot be situated in the benzene ring, whilst it cannot be attached to nitrogen because the substance does not react with diethylamine, diethylaniline, or potassium iodide. When boiled with concentrated hydrochloric acid, it is converted into 4-tetrahydroquinolone. Whilst toluene-*p*-sulphonyl-4-tetrahydroquinolone is converted by methyl-alcoholic potassium hydroxide into an *isomeric substance*, m. p. 135—150°, the corresponding derivative of 3-chloro-4-tetrahydroquinolone forms 4-*methoxyquinoline*, b. p. 167°/20 mm., m. p. 39—40°; *methiodide*, m. p. 145° (decomp.); *chloromercurate*, m. p. 201—202° (decomp.) (cf. Meyer, A., 1906, i, 604). Removal of the toluenesulphonyl group seems to be connected with the presence of the chlorine atom in the β-position adjacent to the carbonyl group; two suggestions as to the mechanism of the reaction are made.

The NH: group of tetrahydroquinolone is in evidence since with nitrous acid it gives *nitroso*-4-*tetrahydroquinolone*, m. p. 98°; it gives a derivative with toluene-*p*-sulphonyl chloride, and with benzoyl chloride gives *benzoyl*-4-*tetrahydroquinolone*, m. p. 122°. The reactivity of the β-CH_2: group is shown by condensation with benzaldehyde in alcoholic solution, in presence of sodium hydroxide, to 3-*benzylidene*-4-*tetrahydroquinolone*, m. p. 214°. The CO: group is reactive and with phenylhydrazine there is formed 4-*tetrahydroquinolonephenylhydrazone*, m. p. 110°. On heating with dilute sulphuric acid, this undergoes the Fischer indole transformation with simultaneous oxidation, yielding 3 : 4-*quinindoline*, which melts and sublimes above 320° (*hydrochloride* and *chloroplatinate* described). When isatin and 4-tetrahydroquinolone are condensed and the product is heated under reduced pressure at

210°, carbon dioxide is eliminated, forming *dihydro*-2 : 3-*quinoquinoline* (I), m. p. 235—237° (softening at 230°), affording fluores-

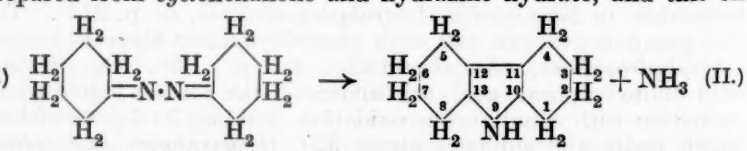


cent solutions. Distillation over lead oxide affords 2 : 3-*quinoquinoline* (II), m. p. 186—187°. Reduction of nitroso-4-tetrahydroquinolone at 35—40° with zinc dust in presence of *cyclo*hexanone gave 1-cyclo*hexylideneamino*-4-*tetrahydroquinolone* (III), m. p. 112°. Dilute sulphuric acid converts this into *tetrahydrocarbazole*-9 : 8-*anhydropropionic acid* (IV), m. p. 135—136°; *phenylhydrazone*, m. p. 191°. 4-Tetrahydroquinolone is reduced by sodium amalgam



to a mixture of 4-*hydroxytetrahydroquinoline*, colourless prisms, m. p. 83—84° (*diacetyl* derivative, m. p. 95—96°), and 4 : 4′-*dihydroxy*-1 : 2 : 3 : 4 : 1′ : 2′ : 3′ : 4′-*octahydro*-4 : 4′-*diquinolyl*, decomp. 235°, clear melt at 260°. This pinacol is dehydrated by concentrated sulphuric acid to 1 : 2 : 1′ : 2′-*tetrahydro*-4 : 4′-*diquinolyl*, m. p. 165° (softening at 155°); *diacetyl* derivative, m. p. 230—231°. On boiling the methyl-alcoholic solution of the pinacol, oxidation occurs to 1 : 2-*dihydro*-4 : 4′-*diquinolyl*, m. p. 210° (softening at 200°); on keeping the solution in contact with air for some days, it yields 4 : 4′-*diquinolyl*, m. p. 166°. F. M. H.

1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-Octahydrocarbazole and its Derivatives. W. H. Perkin, jun., and S. G. P. Plant (*J. Chem. Soc.*, 1924, **125**, 1503—1512).—A detailed study of some of the more highly reduced derivatives of carbazole is described (see also T., 1921, **119**, 1825; 1923, **123**, 676). Catalytic reduction of carbazole by hydrogen in the presence of nickel does not appear to give the desired derivatives (cf. Padoa and Chiaves, A., 1908, i, 104; Von Braun and Ritter, A., 1923, i, 141). *cyclo*Hexylideneazine (I) was prepared from *cyclo*hexanone and hydrazine hydrate, and this on



heating with hydrogen chloride in tetrahydronaphthalene gave a dark red oil. The fraction of b. p. 165—170°/15 mm. solidified

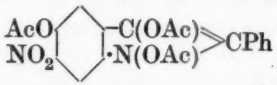
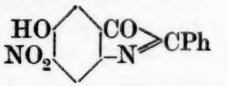
and yielded (28% of the theoretical) 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydrocarbazole* (II), m. p. 102°. The method of synthesis gives the constitution. The *picrate* had m. p. 140°; 9-*acetyloctahydrocarbazole*, m. p. 73°, was easily hydrolysed. Prolonged reduction of the octahydrocarbazole (II) with tin and hydrochloric acid gives 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 10 : 13-*decahydrocarbazole* (III), m. p. 75°, in good yield; *picrate*, m. p. 210° (decomp.). This decahydrocarbazole could not be reduced further in the electrolytic cell. Octahydrocarbazole is completely reduced electrolytically to *dodecahydrocarbazole* (IV), $C_{12}H_{20}NH$, m. p. 65°; *picrate*, m. p. 187°. It is noteworthy that decahydrocarbazole (III) is not reduced to dodecahydrocarbazole by electrolysis. Octahydrocarbazole (II) probably passes into 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 10 : 11-decahydrocarbazole and thence to (IV). Octahydrocarbazole is readily alkylated in alcoholic solution. When boiled under reflux with methyl iodide, it gave 9-*methyloctahydrocarbazole* (V), b. p. 139—140°/14 mm. (70% yield); *picrate*, m. p. 147°; *methiodide*, m. p. 194°. Reduction of (V), whether electrolytically or by tin and hydrochloric acid, produced only 9-*methyldecahydrocarbazole*, b. p. 128°/13 mm.; *picrate*, m. p. 162—163°; a definite methiodide was not obtained. 9-*Methyldodecahydrocarbazole*, b. p. 132°/18 mm., was prepared in good yield by the action of methyl iodide on (IV); *picrate*, m. p. 146°.

9-*Ethyloctahydrocarbazole*, prepared similarly, is a viscous, colourless oil, b. p. 166—170°/20 mm., which gradually turned yellow and then bright red on exposure to air; *picrate*, m. p. 152°; *methiodide*, m. p. 169°. 9-*Ethyldecahydrocarbazole* can be obtained by both of the methods given for the 9-methyl derivative as a colourless liquid, stable in air, b. p. 148—150°/21 mm.; *picrate*, m. p. 202°; *methiodide*, m. p. 205°. 9-*Ethyldodecahydrocarbazole*, by ethylation of dodecahydrocarbazole, has b. p. 143—145°/22 mm.; *picrate*, m. p. 132—133°; *methiodide*, m. p. 217°.

Several of these *N*-alkyl derivatives of the carbazoles were compared with corresponding compounds obtained by Von Braun and Ritter (*loc. cit.*) by catalytic reduction, and found to differ in important particulars: the 9-methyloctahydrocarbazole of Von Braun and Ritter has m. p. 94° and b. p. 176—178°/16 mm. and gives neither a crystalline picrate nor a methiodide (see above). The two compounds are isomerides, and it is suggested that the latter is 9-methyl-1 : 2 : 3 : 4 : 8 : 10 : 11 : 13-octahydro- or, more probably, 9-methyl-1 : 2 : 3 : 4 : 7 : 8 : 10 : 13-octahydrocarbazole, whilst that of the present authors has the true pyrrole structure and is 9-methyl-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrocarbazole. A similar structural difference is suggested for the corresponding isomeric decahydro compounds prepared by the two methods. The electrolytic reduction of tetrahydrocarbazole was found to stop at the hexahydro stage and to give the carbazole (m. p. 99°) in nearly quantitative yield. 9-*Methylhexahydrocarbazole* was obtained by reducing the tetra compound either electrolytically or by tin and hydrochloric acid. It is a colourless liquid, b. p. 144°/15 mm.; *picrate*, m. p. 143—144° (decomp.). A. C.

Sodamide as a Dehydrating Agent. Preparation of Indole, Methylindole, and Homologues. A. VERLEY (*Bull. Soc. chim.*, 1924, [iv], **35**, 1039—1040).—Sodamide readily converts aceto-*o*-toluidide into methylindole by heating at 270°, whereas the ordinary dehydrating agents, even thoria at 450°, fail; some *o*-toluidine is formed. The method is applicable to the preparation of homologues of methylindole. Indole can be obtained from formyl-*o*-toluidide, but the reaction must be moderated by dilution with sand or kieselguhr and the addition of a heavy solvent. R. B.

Hydroxyquinol Derivatives of the Isatogen Series. P. RUGGLI and W. LEONHARDT (*Helv. Chim. Acta*, 1924, **7**, 689—702; cf. A., 1923, i, 833).—6-*Nitro*-1 : 3 : 5-*triacetoxy*-2-*phenylindole*, m. p. 194—195° (I), is produced, together with another compound to be described later, when 6-nitro-2-phenylisatogen is treated with acetic anhydride and sulphuric acid, the action resembling that whereby *p*-benzoquinone is converted into 1 : 2 : 4-triacetoxybenzene. When the triacetoxy compound is heated with dilute alcoholic hydrochloric acid it affords 6-*nitro*-5-*hydroxy*-1 : 3-*diacetoxy*-2-*phenylindole*, m. p. 214—215°, which may be re-acetylated to regenerate its parent, or treated with chloroacetic anhydride to afford 6-*nitro*-1 : 3-*diacetoxy*-5-*chloroacetoxy*-2-*phenylindole*, m. p. 156—158° (decomp.). When the diacetoxy compound is treated with diazomethane, it gives 6-*nitro*-5-*methoxy*-1 : 3-*diacetoxy*-2-*phenylindole*, m. p. 221—222°. The triacetoxy compound dissolves in cold sulphuric acid to form a dark violet-coloured solution from which, on dilution, 6-*nitro*-5-*hydroxy*-3-*keto*-2-*phenylindolenine* (II),

(I.)  (II.) 

cherry-red needles, m. p. 188°, is precipitated. This substance yields an *oxime*, which decomposes at 280°, but when treated with methyl sulphate yields a *methyl* ether, m. p. 172°; this can be acetylated (on the phenolic hydroxyl) to an *acetyl* derivative, m. p. 152°. When 6-nitro-5-methoxy-1 : 3-diacetoxy-2-phenylindole is treated with concentrated sulphuric acid it yields 6-*nitro*-5-*methoxy*-3-*keto*-2-*phenylindolenine*, dark red needles, m. p. 157°; the *oxime*, m. p. 263—264°, can be methylated to a *methyl* derivative, m. p. 157°, which may also be obtained by treatment of the above hydroxy-oxime with an excess of diazomethane. The methoxyoxime is oxidised by chromic–acetic acid to 3 : 6-*dinitro*-5-*methoxy*-2-*phenylindole*, m. p. 303—306° (decomp.), whilst 6-nitro-5-methoxy-3-keto-2-phenylindolenine, the parent ketone, is converted by the same reagent into 4-*nitro*-2-*benzoylamido*-5-*methoxybenzoic acid*, m. p. 272°, which is hydrolysed by syrupy phosphoric acid at 130—170°, 4-*nitro*-2-*amino*-5-*methoxybenzoic acid*, violet needles, m. p. 217—218°, being thus obtained. 4-*Amino*-2-*benzoylamido*-5-*methoxybenzoic acid*, colourless scales, decomp. 200°, is obtained by catalytic reduction (nickel) of the nitro acid, and has an *acetyl* derivative, decomp. 275°; when it is diazotised and treated with cuprous oxide 2-*benzoylamido*-5-*methoxybenzoic acid*, m. p. 200°, is obtained. This

compound was identified by comparison with a sample prepared as follows. *2-Nitro-5-methoxytoluene*, m. p. 50°, is obtained when 6-nitro-*m*-cresol is methylated; it is reduced and forthwith benzoylated yielding *2-benzoylamido-5-methoxytoluene*, colourless needles, m. p. 200°, which, when oxidised with hot dilute potassium permanganate solution, yields 2-benzoylamido-5-methoxybenzoic acid. *2-Benzoylamido-3-methoxybenzoic acid*, obtained *via* 2-nitro-3-methoxybenzoic acid, has m. p. 204·5°, and *2-benzoylamido-6-methoxybenzoic acid* has m. p. 120°. The latter compound was prepared from 6-nitro-*o*-cresol; *2-nitro-6-methoxytoluene* has m. p. 52° and when reduced and benzoylated yields *2-benzoylamido-6-methoxytoluene*, m. p. 177°.

When 6-nitro-5-methoxy-1 : 3-diacetoxy-2-phenylindole is treated with stannous chloride in acetic acid solution *6-amino-5-methoxy-3-acetoxy-2-phenylindole*, m. p. 212°, is obtained, and this is converted by acetic anhydride and sulphuric acid into a *diacetyl* derivative, m. p. 220°.

When methyl isatogenate (Pfeiffer, A., 1916, i, 327) is treated with acetic anhydride and a little sulphuric acid a *compound*, m. p. 193—195°, possibly analogous to the one described above, is obtained.

W. A. S.

Action of Oxalyl Chloride on certain Cyclic Organic Bases. M. Giua (*Gazzetta*, 1924, **54**, 593—597; cf. Oddo and Sanna, A., 1922, i, 371).—When oxalyl chloride and pyrrole interact below 0° and the mass is subsequently heated on a water-bath, black pigments are formed, together with 2-pyrrylglyoxyl chloride, which yields the acid (cf. Ciamician and Silber, A., 1884, 1044, 1193) in presence of water. From indole an almost theoretical yield of 2-indoleglyoxyl chloride is obtained in absolute ethereal solution, the corresponding acid being obtained by treatment with water; 2-methyl-3-indoleglyoxyl chloride and a magenta colouring matter are obtained similarly from 2-methylindole.

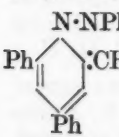
2-Indoleglyoxyl chloride, $C_6H_4\langle\begin{matrix}CH\\NH\end{matrix}\rangle C\cdot CO\cdot COCl$, has m. p. 138—139°. *2-Indoleglyoxylic acid*, $C_8H_6N\cdot CO\cdot CO_2H$, m. p. 224—225° (decomp.), when treated with fused potassium hydroxide at 200—205° yields indole-2-carboxylic acid. *Silver 2-indoleglyoxylate* forms white crystals.

2-Methyl-3-indoleglyoxyl chloride forms a brown, crystalline mass and, when heated with neutral solvents, resinifies and yields a magenta-red substance. 2-Methyl-3-indoleglyoxylic acid (cf. Angeli and Marchetti, A., 1908, i, 207) forms a *methyl* ester, m. p. 172—173°. The *colouring matter* formed together with the chloride separates as a dark red powder, m. p. about 120°, decomposes at a slightly higher temperature, dissolves readily in concentrated acids or in alkali solution, and contains 8·22% of nitrogen. T. H. P.

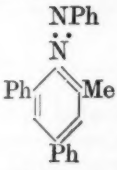
Pyridine-arylimines. I. W. Schneider [with W. Doenhardt, O. Süssenguth, H. Nitzsche, A. Ross, A. Sack, and E. Leutheusser] (*Annalen*, 1924, **438**, 115—146).—*1 : 4 : 6-Triphenyl-2-methylpyridinium iodide*, m. p. 243°, is obtained by treating

4 : 6-diphenyl-2-methylpyrylium iodide with aniline (cf. Schneider and Seebach, A., 1921, i, 877; Schneider and Ross, A., 1922, i, 1171); when treated with alkali, the corresponding anhydro base, 1 : 4 : 6-*triphenyl-2-methylenedihydropyridine*, is produced as an unstable, reddish-brown, amorphous substance; this combines instantly, when freshly isolated, with carbon disulphide to yield a dark red *substance*, $C_{50}H_{40}O_2N_2S_3$, m. p. 200° (cf. Schneider, Gaertner, and Jordan, this vol., i, 551), which gives a *perchlorate*, m. p. 170°. The anhydro base also combines with phenylthiocarbimide, affording a red *compound*, $C_{24}H_{19}N,Ph{\cdot}NCS$, and with phenylcarbimide, an analogous *compound*, red prisms, m. p. 233°, being produced. 4 : 6-*Diphenyl*-1-*benzyl*-2-*methylpyridinium iodide*, similarly produced from benzylamine and the pyrylium iodide, has m. p. 212°. The corresponding base is again a brown, amorphous substance reacting with the above three reagents; with carbon disulphide a red *compound*, with phenylthiocarbimide a *compound*, red needles, m. p. 193°, and with phenylcarbimide a similar *product*, m. p. 195°, are obtained. 1-*Methylamino*-4 : 6-*diphenyl*-2-*methylpyridinium iodide*, obtained when methylhydrazine is used, forms yellow needles, m. p. 180°. Its anhydro *base* is very unstable; with carbon disulphide it affords a red substance and with phenyl-carbimide and -thiocarbimide greenish-yellow (m. p. 242°) and red (m. p. 164°) *compounds*, respectively. 1-*Phenylmethylamino*-4 : 6-*diphenyl*-2-*methylpyridinium iodide*, obtained by using *as*.-phenylmethylhydrazine, is an orange-yellow substance, m. p. 167°, and gives a yellow, amorphous *base* which, like its congeners, reacts with carbon disulphide and phenylcarbimide, but gives a definite *compound* (red needles, m. p. 171°) only with phenylthiocarbimide. Similarly, 1-*diphenylamino*-4 : 6-*diphenyl*-2-*methylpyridinium iodide* (yellow crystals, m. p. 137°) affords a yellow, amorphous *base*, very unstable, the phenylthiocarbimide *compound* of which forms dark red leaflets, m. p. 124°.

The characteristic properties of the methylenedihydropyridines are illustrated by the above examples. To the blue base obtained by Schneider and Seebach (*loc. cit.*) an analogous constitution was originally ascribed; certainly in some reactions it behaves as if it were 1-phenylamino-4 : 6-diphenyl-2-methylenedihydropyridine, but in other respects it is quite different from the above compounds of this class. Thus, it combines with phenylcarbimide, but with two molecular proportions, to form the *compound* $C_{38}H_{30}N_4O_2$, m. p. 128·4°; it also reacts with carbon disulphide, but slowly (cf. *loc. cit.*); it yields an *acetyl* derivative, an amorphous mass, resembling the above bases, which again combines with phenylcarbimide to a *compound*, m. p. 150° (annexed formula), and when treated with ammoniacal silver nitrate it forms a red complex *salt*, $(C_{24}H_{20}N_2)_2,AgNO_3$, m. p. 168°. On the other hand, the base is intensely blue and crystalline; when treated with methyl iodide it yields, as one product, the 1-phenylmethylamino-4 : 6-diphenyl-2-methylpyridinium iodide described above; its colour depends on



the solvent used to dissolve it, and its stability on the same factor; thus it is blue in benzene or chloroform and loses its colour in a few hours, but in alcohol it is violet and tolerably stable. Experiments are described in which the action of nitrous acid and nitric oxide on this base and on its congeners described below was investigated, but these gave no conclusive results. As the base obtained from 1-methylamino-4 : 6-diphenyl-2-methylpyridinium iodide, described above, resembles its congeners, in this blue base the presence of the phenyl group in place of the methyl is considered so to affect the valency distribution that the compound should be formulated as a pyridinephenylimine (annexed formula), being thus the first member of a new class of compounds. This explains satisfactorily the blue colour of the substance, and the properties wherein it resembles the methylene anhydro bases can be referred to tautomeric change.



Phenylhydrazine and 2 : 6-diphenyl-4-methylpyrylium iodide (Schneider and Ross, *loc. cit.*) yield, in cold alcohol solution with a little acetic acid, 1-*phenylamino*-2 : 6-*diphenyl*-4-*methylpyridinium iodide*, yellow needles, m. p. 200°. When this is treated with sodium hydroxide, 2 : 6-*diphenyl*-4-*methylpyridinephenylimine*, a deep blue substance, needles, m. p. 101°, closely resembling its isomeride, is obtained. This reacts with carbon disulphide and phenylthiocarbimide, and with phenylcarbimide forms an orange *compound* crystallising in leaflets, m. p. 152°. It also yields a complex *salt* with silver nitrate, m. p. 172°.

2 : 4 : 6-Triphenylpyrylium iodide (Schneider and Seebach, *loc. cit.*) and phenylhydrazine react in cold alcohol to give (α-) 2 : 4 : 6-*triphenylpyranol phenylhydrazide* (cf. following abstract), m. p. 162°, but in hot alcohol an isomeride, the (β-)*hydrazide*, m. p. 126°, is obtained. When the α-hydrazide is treated with hot acetic acid, and the solution basified, it is converted chiefly into 2 : 4 : 6-*triphenylpyridinephenylimine*, dark blue needles, m. p. 182°. This compound resembles its congeners, but is more stable, reacts more slowly, and gives less well-defined products with the customary reagents. When it is treated in dilute acetic acid solution with potassium iodide, 1-*phenylamino*-2 : 4 : 6-*triphenylpyridinium iodide*, yellow needles, m. p. 161°, is obtained, whilst with methyl iodide it yields 1-*phenylmethylamino*-2 : 4 : 6-*triphenylpyridinium iodide*, m. p. 136°, identical with the product of interaction of phenylmethylhydrazine and the pyrylium iodide. The corresponding amorphous anhydro *base* appears to suffer conversion into a *phenylhydrazide*, m. p. 160°, when recrystallised from alcohol (cf. following abstract). W. A. S.

Reaction of Pyrylium Compounds with Phenylhydrazine. W. Schneider and W. Müller (*Annalen*, 1924, **438**, 147—154).—When 4 : 6-diphenyl-2-methylpyrylium iodide or sulphoacetate (cf. preceding abstract and earlier references quoted therein) is treated with phenylhydrazine in cold alcoholic solution, the α-phenylhydrazide, 4 : 6-*diphenyl*-2-*methylpyranolphenylhydrazide*, yellow

needles, m. p. 119°, is obtained. In this compound, the pyranol ring is considered to remain intact. It is a comparatively unstable substance; even when dissolved in cold acetic acid it is partly decomposed to the parent pyrylium compound, and partly converted into a 1-phenylamino-4 : 6-diphenyl-2-methylpyridinium salt, whilst with alkali 4 : 6-diphenyl-2-methylpyridinephenylimine is obtained. With phenylhydrazine, or if the pyrylium salt be directly treated with an excess of phenylhydrazine, further interaction takes place, producing the *phenylhydrazone*,

NHPh·N:CPh·CH:CPh·CH:CMe·NH·NHPh,

orange needles, m. p. 130°.

When the original alcoholic reaction mixture is heated, an isomeride, the β-*hydrazide*, is produced. This is also obtained when an alcoholic solution of the α-compound is heated for some time. It forms stable, brownish-yellow crystals, m. p. 115°. The pyranol ring is supposed here to have become opened up, but the authors have not yet decided which of the numerous possible formulæ should be attributed to the compound. It is only converted into the pyridinium salt by long treatment with acetic acid. When it is treated with phenylhydrazine, it yields a *phenylhydrazone* isomeric with that described above, yellow needles, m. p. 178°.

W. A. S.

4-Benzyl-2-methylquinoline. E. Rosenhauer (*J. pr. Chem.*, 1924, [ii], **108**, 91—98).—4-*Benzyl*-2-*methylquinoline*, obtained by heating *N*-benzylquinaldinium iodide at 230°, has m. p. 63°; *picrate*, decomp. 185°; *hydrochloride*, decomp. 216°; *hydriodide*, decomp. 234°; *methiodide*, decomp. 194°. The base reacts with benzaldehyde, forming 4-*benzyl*-2-*styrylquinoline*, m. p. 99°; *picrate*, decomp. 237°; *hydrochloride*, decomp. 231°; *methiodide*, decomp. 224°. The methiodide when heated with alcoholic potassium hydroxide loses hydrogen iodide, forming 1-*methyl*-4-*benzylidene*-2-*styryl*-1 : 4-*dihydroquinoline*, brick-red needles, m. p. 140°.

4-*Benzyl*-2-p-*dimethylaminostyrylquinoline* forms yellow prisms, m. p. 158°; its halogen acid salts, which are dyestuffs, are of uncertain composition; the *picrate*, decomp. 239°, and *methiodide*, decomp. 261°, giving an intensely red alcoholic solution, were prepared. 4-*Benzyl*-2-m-*nitrostyrylquinoline*, crystals, m. p. 182°, forms a *picrate*, decomp. 217°. 4-*Benzylquinophthalone*, from 4-benzylquinaldine and phthalic anhydride, forms yellow needles, m. p. 236°.

E. H. R.

Aryl Substituted Aminoquinolines and their Derivatives. M. Dohrn, C. Zöllner, and Chemische Fabrik auf Aktien (vorm. E. Schering) (D.R.-P. 375715; from *Chem. Zentr.*, 1924, i, 967—968).—2-Arylquinoline-4-carboxylamides are treated with salts of hypohalogenous acids at low temperatures. The following compounds are mentioned: 4-*Amino*-2-*phenylquinoline*, m. p. 165°; 4-*amino*-2-*phenyl*-6-*methylquinoline*, m. p. 188—189°; 4-*amino*-2 : 2′-*chlorophenylquinoline*, m. p. 166°; 2 : 2′-*chlorophenylquinoline*-4-*carboxylamide*, m. p. 228—229°; 2 : 2′-*chlorophenylquinoline*-4-*carboxylic* acid, m. p. 256—257°; 2 : 4′-*chloro*-

phenylquinoline-4-carboxylic acid, m. p. 228—229°; 2 : 4′-*chlorophenylquinoline-4-carboxylamide*, m. p. 238°; and 4-*amino*-2 : 4′-*chlorophenylquinoline*, m. p. 150—151°. G. W. R.

Production of Acridinium Compounds. L. CASSELLA und Co. (Brit. Pat. 218542).—Hydroxy- and alkoxy-acridines are converted into acridinium compounds by the action of alkylating agents, such as methyl and ethyl *p*-toluenesulphonates, benzyl chloride, and ethylene chlorohydrin, in absence of bases, as, for example, in hot nitrobenzene solution. 3 : 6-*Dihydroxy*-10-*methylacridinium chloride*, yellow needles; 3 : 6-*dimethoxy*-10-*methylacridinium chloride*, light yellow scales; 3 : 6-*dimethoxy*-10-*ethylacridinium chloride*, orange-yellow scales, m. p. 198° (decomp.); 3 : 6-*dimethoxy*-10-*benzylacridinium chloride*, dark yellow needles, m. p. 236° (decomp.); and 3 : 6-*dimethoxy*-10-*hydroxyethylacridinium chloride*, pale yellow needles, m. p. 240—242°, are described, all of which are strong bactericides of low toxicity and slight tinctorial power. F. G. W.

Preparation of Colouring Matters. AKTIEN-GESELLSCHAFT FÜR ANILIN FABRIKATION (W. HERZBERG, and G. HOPPE) (D.R.-P. 384790; from *Chem. Zentr.*, 1924, i, 1110—1111).—The following compounds are mentioned: *hydroxynaphthacridine*, orange-yellow; its *hydrochloride*, yellow; and *dihydroxydinaphthacridine*, orange. G. W. R.

Unsymmetrical *CC*-Dialkylbarbituric Acids. E. LAYRAUD (Fr. Pat. 546997; from *Chem. Zentr.*, 1924, i, 2205; cf. this vol., i, 92—93).—The following compounds, obtained by alkylation of the silver compounds of monoalkylbarbituric acids, are described: *ethylbutylbarbituric acid*, m. p. 126—127°; *butylallylbarbituric acid*, m. p. 118°. G. W. R.

Unsymmetrical *CC*-Dialkylbarbituric Acids and their Salts. E. LAYRAUD (Fr. Pat. [Add.] 26209; from *Chem. Zentr.*, 1924, i, 2205—2206; cf. preceding abstract).—The following new compound is mentioned: *piperazine ethylbutylbarbiturate*, m. p. 150—155°. G. W. R.

Bromo Derivatives of 1-Methylglyoxaline and Constitution of "Chloroxalmethylin." I. E. BALABAN and F. L. PYMAN (*J. Chem. Soc.*, 1924, **125**, 1564—1572).—The bromination of 1-methylglyoxaline resembles that of glyoxaline (cf. T., 1922, **121**, 947). The main product is 2 : 4 : 5-tribromo-1-methylglyoxaline, m. p. 93—94·5° (*hydrochloride*, prisms, m. p. 190—200°). The second product was proved to be 4 : 5-*dibromo*-1-*methylglyoxaline*, m. p. 79—80°, by its preparation from 4 : 5-dibromoglyoxaline and methyl sulphate (*hydrochloride*, m. p. 179°, with previous softening [*dihydrate* also described], *nitrate*, m. p. 153°, *picrate*, m. p. 148—149°). Unlike the unmethylated base, 2 : 4 : 5-tribromo-1-methylglyoxaline is resistant to the action of sodium sulphite, so 4(or 5)-bromo-1-methylglyoxaline cannot be thus prepared. 5-*Bromo*-1-*methylglyoxaline*, b. p. 128°/*ca.* 15 mm.,

m. p. 45—46°, is obtained (yield 51%), together with 4-*bromo*-1-*methylglyoxaline* (yield 1·5%), by the action of methyl sulphate on 4(or 5)-bromoglyoxaline; the *hydrochloride* (losing $\frac{1}{2}H_2O$), m. p. 155°; *nitrate*, m. p. 155°; *hydrogen oxalate* (losing $\frac{1}{2}H_2O$), m. p. 147°; *picrate*, m. p. 190°, are described. Its nitration and sulphonation (as for 4-bromoglyoxaline, *loc. cit.*) gave 5-*bromo*-4-*nitro*-1-*methylglyoxaline* (yield 80%), m. p. 180° (*hydrochloride*, m. p. about 155°), and 5-*bromo*-1-*methylglyoxaline*-4(?)-*sulphonic acid* (yield 78%), m. p. 284°, hydrolysed to 5-*bromo*-1-*methylglyoxaline*. 5-Bromo-1-methylglyoxaline is converted by formaldehyde at 130° into 5-*bromo*-2-*hydroxymethyl*-1-*methylglyoxaline* (yield 42%), m. p. 143° (*picrate*, m. p. 165—166°). Reduction with hydriodic acid and phosphorus gave 1 : 2-dimethylglyoxaline (cf. Windaus, A., 1909, i, 258). Interaction of *sym.*-dimethyloxamide and phosphorus pentabromide gave 4 : 5-*dibromo*-1-*methylglyoxaline*. Contrary to the conclusion of Sarasin (A., 1923, i, 710), the product (chloroxalmethylin) of the interaction of *sym.*-dimethyloxamide and phosphorus pentachloride (Wallach, A., 1877, ii, 182) is found to be 5-*chloro*-1-*methylglyoxaline* and the isomeric base produced by distillation of its methiodide must therefore be 4-*chloro*-1-*methylglyoxaline*. The action of methyl iodide on 4(or 5)-bromo-1-methylglyoxaline gave 4(or 5)-*bromo*-1 : 3-*dimethylglyoxalinium iodide*, m. p. 202—204°, which by distillation in a vacuum yielded 4-*bromo*-1-*methylglyoxaline nitrate*, m. p. 155° (yield 43%); the *base* itself was an oil (*picrate*, m. p. 179°). Nitration and sulphonation of 4-bromo-1-methylglyoxaline gave 4-*bromo*-5-*nitro*-1-*methylglyoxaline* (yield 54%), m. p. 105°, this being the main product of the action of methyl sulphate on 4(or 5)-bromo-5(or 4)-nitroglyoxaline; 4-*bromo*-1-*methylglyoxaline*-5(?)-*sulphonic acid* (yield 77%), prisms ($+1H_2O$), m. p. 256° (decomp.), is hydrolysed to 4-*bromo*-1-*methylglyoxaline*.

4(or 5)-Bromoglyoxaline does not react with bromobenzene or sodium sulphite, but is reduced by hydriodic acid and phosphorus to glyoxaline. The reactivity of the halogen is increased by the presence of an *o*-nitro group. Thus 4(or 5)-bromo-5(or 4)-nitroglyoxaline on boiling with aqueous sodium sulphite gave 5(or 4)-*nitroglyoxaline*-4(or 5)-*sulphonic acid* (yield 88%), decomp. 300° (*sodium* salt described). The orientation of 5-chloro-(or bromo)-1-methylglyoxaline was established directly and that of 4-bromo-1-methylglyoxaline indirectly: "Chloroxalmethylin" *nitrate*, m. p. 145°, on heating with concentrated sulphuric acid, gave 5-*chloro*-4-*nitro*-1-*methylglyoxaline* (yield 71%), m. p. 147°. From 5-chloro-(or bromo)-4-nitro-1-methylglyoxaline was obtained 4-*nitro*-1-*methylglyoxaline*-5-*sulphonic acid*, m. p. 254° (*sodium* salt described). The latter was hydrolysed by 30% aqueous sulphuric acid at 170° to 4-*nitro*-1-*methylglyoxaline*. F. M. H.

Tautomerism of Amidines. IV. Methylation of 4(or 5)-Nitroglyoxaline and 4(or 5)-Phenylglyoxaline. C. E. Hazeldine, F. L. Pyman, and (the late) J. Winchester (*J. Chem. Soc.*, 1924, **125**, 1431—1441).—The action of methyl sulphate on nitro-

and phenyl-substituted glyoxalines has been studied and the proportions of the two isomeric alkyl derivatives have been determined (cf. T., 1923, **123**, 3359). Glyoxalines having the nitro group in the 4(or 5)-position invariably yield the 5-nitro-1-methyl derivative as main product. The methylation of 4(or 5)-nitroglyoxaline leads to 5-nitro- and 4-nitro-1-methylglyoxalines in the proportions 350 : 1 (cf. also T., 1922, **121**, 2616; 1923, **123**, 494). The influence of the bromine atom is similar to, but not so powerful as that of the nitro group, the proportions for similar bromo-substituted compounds being 34 : 1. Substituents of negative polarity, methyl and cyanomethyl (cf. T., 1923, **123**, 367), act in the opposite way. The influence of phenyl as substituent is exceptional and 4(or 5)-phenylglyoxaline yields on methylation 4-phenyl- and 5-phenyl-1-methylglyoxaline in the proportions 4·8 : 1. On the other hand, the phenyl group affects the results of the distillation of the common methiodides in the same way as a nitro or bromo group. This abnormality may be ascribed more to the structure of the molecule than to its polarity. The orientation of the 4- and 5-nitro-1-methylglyoxalines was determined by the method used for the nitro-1 : 4- and -1 : 5-dimethylglyoxalines (cf. T., 1922, **121**, 2616). The differences in physical properties of the two monomethylnitroglyoxalines are paralleled by the above dimethyl derivatives. 4-*p*-Nitrophenyl- and 5-*p*-nitrophenyl-1-methylglyoxalines were obtained on nitrating the corresponding phenylmethylglyoxalines, the positions of the nitro groups being proved by the formation of a mixture of the two bases by the methylation of 4(or 5)-*p*-nitrophenylglyoxalines (T., 1921, **119**, 1893). Further nitration resulted in the formation of 5-nitro-4-*p*-nitrophenyl-1-methylglyoxaline, for which the position of the second nitro group was found by methylation of 4(or 5)-nitro-5(or 4)-*p*-nitrophenylglyoxaline. The dinitro base on reduction gave 5-amino-4-*p*-aminophenyl-1-methylglyoxaline, which on hydrolysis yielded *p*-aminophenylaminoacetic acid, methylamine, and ammonia. The relative positions of the methyl and phenyl groups follow from this. 4(or 5)-Nitroglyoxaline was methylated by treatment with methyl sulphate at 100° and yielded 63·4% of the theoretical of the 5-nitro to 0·24% of the 4-nitro compound. By nitration of 1-methylglyoxaline, 21% of the theoretical of the 4-nitro to 8% of the 5-nitro compound was obtained. 4-*Nitro*-1-*methylglyoxaline* has m. p. 133—134°; the *hydrochloride* yields the base when heated at 100°. 5-*Nitro*-1-*methylglyoxaline* has m. p. 55°; the *hydrochloride*, after drying at 100°, has m. p. 195° (effervescence); *picrate*, m. p. 153·5°. Reduction of 5-nitro-1-methylglyoxaline by stannous chloride gave methylamine, ammonia, and glycine ethyl ester as hydrochlorides. 4(or 5)-*Nitro*-1 : 3-*dimethylglyoxalinium iodide*, m. p. 181° (effervescence), was obtained by heating 5-nitro-1-methylglyoxaline with methyl iodide. By the action of methyl sulphate on 4-phenylglyoxaline in the cold and completion at 100°, a product was obtained from which (after the removal of unchanged material as nitrate) the 4-phenyl- and 5-phenyl-1-methylglyoxalines were separated as picrates (yields, 29·8 and

6·2% of the theoretical). 4-*Phenyl*-1-*methylglyoxaline* has m. p. 110—111°; the *hydrobromide* ($+1H_2O$) has m. p. 178—179°; *nitrate*, m. p. *ca.* 97°; *picrate*, m. p. 245°, microscopic needles. 5-*Phenyl*-1-*methylglyoxaline*, m. p. 96—97°, plates; *nitrate*, m. p. 176—177° (decomp.); *picrate*, m. p. 139°. 4(or 5)-*Phenyl*-1 : 3-*dimethylglyoxalinium iodide* forms colourless prisms, m. p. 147—148°. Nitration of 4-phenyl-1-methylglyoxaline took place on heating a solution of the nitrate in concentrated sulphuric acid at 100°. The chief product (56% of the theoretical yield) was 4-p-*nitrophenyl*-1-*methylglyoxaline*, pale yellow prisms, m. p. 195°. It forms a *nitrate*, cream-coloured, woolly needles, m. p. 197° (decomp.), and a *picrate*, m. p. 258°, microscopic needles. The nitrate of an isomeric base, presumably 4-o-*nitrophenyl*-1-*methylglyoxaline*, flat, colourless prisms, decomp. 182°, was formed in considerable amount and also a small amount of a dinitro derivative. 5-p-*Nitrophenyl*-1-*methylglyoxaline*, lemon-yellow needles, m. p. 171—172°, forms a *nitrate*, colourless plates, m. p. 213° (decomp.), and *picrate*, prismatic needles, m. p. 184°. Methylation of 4-*p*-nitrophenylglyoxaline gave 4-*p*-nitro- and 5-*p*-nitro-phenyl-1-methylglyoxalines in yields of 28 and 2·6% of the theoretical, respectively. 5-*Nitro*-4-p-*nitrophenyl*-1-*methylglyoxaline*, m. p. 208—209°, was made by warming the nitrate of the mononitro compound with concentrated sulphuric acid (*hydrochloride* described). 4-*Nitro*-5-p-*nitrophenyl*-1-*methylglyoxaline*, m. p. 187°, is similar in solubility to the 5-nitro compound. Methylation of 5-nitro-4-*p*-nitrophenylglyoxaline yielded 66% of crude methylated product, consisting mainly of 5-nitro-4-*p*-nitrophenyl-1-methylglyoxaline; none of the 4-nitro-5-*p*-compound could be isolated. Reduction of 5-nitro-4-*p*-nitrophenyl-1-methylglyoxaline by stannous chloride gave 68% of the theoretical yield of 5-*amino*-4-p-*aminophenyl*-1-*methylglyoxaline dihydrochloride*, which darkens above 200°. It is readily soluble in water. Aqueous solutions give a transient indigo colour with ammonia, reduce ammoniacal silver nitrate, and give a magenta solution with ferric chloride. On hydrolysis with concentrated hydrochloric acid at 170°, *p*-aminophenylaminoacetic acid dihydrochloride, ammonium chloride, and methylamine hydrochloride were obtained. A. C.

Synthesis of Heteroxanthine from an Iminazole [Glyoxaline] Derivative. J. Sarasin and E. Wegmann (*Helv. Chim. Acta*, 1924, **7**, 713—719).—5-Chloro-1-methylglyoxaline [the 4-chloro-1-methylglyoxaline of Sarasin (A., 1923, i, 710, 711), the present investigation having shown that the names should be interchanged] is converted into the nitrate and this salt treated with concentrated sulphuric acid, whereupon 5-*chloro*-4-*nitro*-1-*methylglyoxaline*, m. p. 147—148°, is obtained. Reduction, or reduction followed by hydrolysis, of this substance gives abnormal results. When it is treated with potassium cyanide and a little potassium iodide in hot alcoholic solution, 4-*nitro*-5-*cyano*-1-*methylglyoxaline*, m. p. 141—142°, is obtained. This product is converted by the action of sulphuric acid into the *amide*, m. p. 257—258° (decomp.), of

4-nitro-1-methylglyoxaline-5-carboxylic acid, m. p. 160° (decomp.), the latter being obtained by alkaline hydrolysis of the amide, this being unaffected by boiling hydrochloric acid. At 120°, however, hydrolysis and decarboxylation take place, and *4-nitro-1-methylglyoxaline*, m. p. 133—134°, is obtained. This is reduced by tin and hydrochloric acid, yielding a *hydrochloride*, presumably of *4-amino-1-methylglyoxaline*, which, when heated with hydrochloric acid at 150°, is broken up into ammonia, a little methylamine, and sarcosine, identified as hydrochloride, m. p. 168—169°. The amide of 4-nitro-1-methylglyoxalinecarboxylic acid is reduced to the *amide*, m. p. 184—185°, of *4-amino-1-methylglyoxaline-carboxylic acid*, the *hydrochloride* of the amide having m. p. 214—215°. This amino-amide reacts at 160—170° with ethyl carbonate to yield heteroxanthine (7-methylxanthine), m. p. 380° (decomp.), identical with the product obtained from theobromine.

4-Chloro-1-methylglyoxaline (*loc. cit.*) is also readily nitrated, yielding *4-chloro-5-nitro-1-methylglyoxaline*, m. p. 77—78°. W. A. S.

Quaternary Salts of Iminazoles [Glyoxalines]. II. J. Sarasin and E. Wegmann (*Helv. Chim. Acta*, 1924, **7**, 720—723; cf. A., 1923, i, 710, 711).—5-Chloro-2-methyl-1-ethylglyoxaline, the constitution of which follows from that of 5-chloro-1-methylglyoxaline (cf. preceding abstract), forms a *methiodide*, m. p. 202—203°, which, when heated in a vacuum at 240°, is broken up into ethyl iodide and *4-chloro-1 : 2-dimethylglyoxaline*, m. p. 93—94°, b. p. 258—260° (*picrate*, m. p. 167—168°), which, when reduced with sodium and alcohol, affords 1 : 2-dimethylglyoxaline. Similarly, *5-chloro-2-methyl-1-ethylglyoxaline ethiodide*, m. p. 142—143°, yields *4-chloro-2-methyl-1-ethylglyoxaline*, b. p. 263—265° (*picrate*, m. p. 154—155°), which on reduction yields 2-methyl 1-ethylglyoxaline; the *propiodide*, m. p. 108—109°, affords *4-chloro-2-methyl-1-propylglyoxaline*, b. p. 135—137°/12 mm. (*picrate*, m. p. 152—153°), and, thence, *2-methyl-1-propylglyoxaline*, b. p. 222—223° (*picrate*, m. p. 142—143°); the iso*butiodide* affords *4-chloro-2-methyl-1-isobutylglyoxaline*, b. p. 144—146°/12 mm. (*picrate*, m. p. 141—142°), and *2-methyl-1-isobutylglyoxaline*, b. p. 225—226° (*picrate*, m. p. 151—152°); the iso*amiodide*, m. p. 133—134°, yields *4-chloro-2-methyl-1-isoamylglyoxaline*, b. p. 153—155°/12 mm. (*picrate*, m. p. 120—121°), and *2-methyl-1-isoamylglyoxaline*, b. p. 242—243° (*picrate*, m. p. 148—149°).

When the nitrate of 5-chloro-2-methyl-1-ethylglyoxaline is heated with sulphuric acid, *4-nitro-5-chloro-2-methyl-1-ethylglyoxaline*, m. p. 88°, is obtained. *5-Nitro-4-chloro-2-methyl-1-ethylglyoxaline*, m. p. 67°, is prepared in a similar way. W. A. S.

Compound of Antipyrine with Trichloroacetic Acid. L. Debucquet (*J. Pharm. Chim.*, 1924, **30**, 121—122).—*Antipyrine trichloroacetate*, $C_{11}H_{12}ON_2,CCl_3{\cdot}CO_2H$, forms lustrous plates, m. p. 79—80°, and is dissociated in aqueous solution. W. T. K. B.

4-Dimethylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone. Chemische Fabrik Altstetten Aktien-Ges. (Swiss Pat. 99452; from *Chem. Zentr.*, 1924, i, 1272).—*4-Dimethylamino-1-phenyl-*

2 : 3-*dimethyl*-5-*pyrazolone* is prepared from 4-*sulphamino*-1-*phenyl*-2 : 3-*dimethyl*-5-*pyrazolone* by the action on it of formaldehyde in the presence of formic acid. G. W. R.

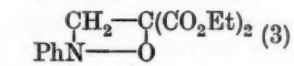
Synthesis of 1 : 2 : 4-Triazole Compounds. VIII. Benzoylformhydroxamic Acid and its Derivatives. C. GASTALDI (*Gazzetta*, 1924, **54**, 582—589).—As would be expected from the synthesis of 1 : 2 : 4-triazole compounds from the arylhydrazones of pyruvylhydroxamic acid (A., 1923, i, 1236), benzoylformhydroxamic acid, Bz·CO·NH·OH or OH·CBz:NOH, is converted quantitatively into benzamide and carbon dioxide when heated at its melting point, this reaction being apparently characteristic of free hydroxamic acids, having the grouping ·CO·CO·NH·OH or ·CO·C(OH):NOH; in the above instance, the formation of benzoylcarbimide as an intermediate compound was assumed, the reaction then proceeding thus: $NBz:C:O+H_2O \longrightarrow NHBz\cdot CO_2H \longrightarrow NH_2Bz+CO_2$ (cf. A., 1923, i, 1237).

Triazole compounds and benzamide may be obtained by heating at the melting point the acyl derivatives of the arylhydrazones of hydroxamic acids and benzoylformhydroxamic acid, respectively. In these cases, the reaction is determined by the temperature, and may be effected also by heating the acids in neutral solvents of high boiling point, such as naphthalene or α- or β-methylnaphthalene. If these solvents are replaced by aniline, the symmetrical disubstituted carbamides are formed, the intermediate formation of carbimides being thus proved: (1) $NPhMe\cdot N:CMe\cdot CO\cdot NH\cdot OAc+NH_2Ph \longrightarrow NPhMe\cdot N:CMe\cdot N:C:O+NHPhAc+H_2O \xrightarrow{+NH_2Ph} NPhMe\cdot N:CMe\cdot NH\cdot CO\cdot NHPh \xrightarrow{+NH_2Ph} NPhMe\cdot N:CMe\cdot NH_2+NHPh\cdot CO\cdot NHPh$. (2) $Ph\cdot CO\cdot CO\cdot NH\cdot OH \xrightarrow{-H_2O} Ph\cdot CO\cdot N:C:O \xrightarrow{+NH_2Ph} Ph\cdot CO\cdot NH\cdot CO\cdot NHPh$.

s.-Diphenylcarbamide is formed by the action of aniline on the acetyl derivative of pyruvylhydroxamic acid phenylmethylhydrazone (cf. A., 1923, i, 1237). s.-*Benzoylphenylcarbamide*, NHBz·CO·NHPh, has m. p. 207°. The *sodium* and *silver* salts of benzoylformhydroxamic acid are described. T. H. P.

Additive Formation of Four-membered Rings. V. Formation of Stable Dimethylene-1 : 2-oxaimines from Ethylenes and Nitroso Compounds, with Special Reference to the Direction of the Addition. C. K. INGOLD and S. D. WEAVER (*J. Chem. Soc.*, 1924, **125**, 1456—1462).—The compounds described are derivatives of the dimethyleneoxaimine ring: $\begin{matrix} C-O \\ | \quad | \\ C-N \end{matrix}$ (cf. this vol., i, 322, 323; also T., 1922, **121**, 2793; 1923, **123**, 2745), which have been produced by the additive union of unsaturated molecules—in the present case an ethylene derivative and a nitroso compound (C:C+N:O). To ensure the stability of this type of ring, it was found desirable to have a bulky *gem*-grouping attached to one of the ring-bound carbon atoms. The *gem*-substituted ethylenes, (1) $CH_2:C(CO_2Et)_2$ and (2) $CH_2:CPh_2$, were employed

in the formation of these rings, which were found to be amongst the most stable four-membered heterocyclic rings yet produced. The direction of the addition of (1) or (2) with nitrosobenzene was found to be at variance with that required by the "theory of alternate polarities" (cf. Lowry, T., 1923, **123**, 822). Thus the ethylene derivative (1) combines readily with nitroso compounds to form rings of the type (3) and not (4), which should not be the case if oxygen key-atoms determine the polarities: $Ar\cdot\overset{+}{N}\overset{-}{:}O$; $\overset{-}{C}H_2\overset{+}{:}C(\overset{+}{C}O_2Et)$.



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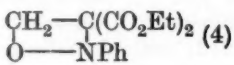

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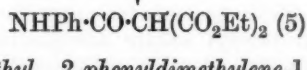

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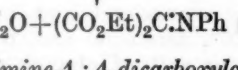
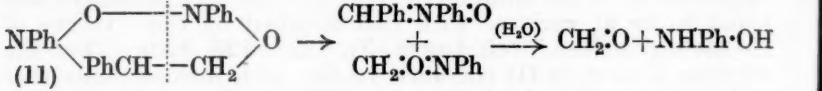


(6)

Ethyl 2-*phenyldimethylene*-1 : 2-*oxaimine*-4 : 4-*dicarboxylate* (3), colourless needles, m. p. 98—100°, was obtained when nitrosobenzene in chloroform was added to ethyl methylenemalonate. It exhibits no salt formation with either strong acids or alkalis; it gives no colour with ferric chloride, no copper salt, and is oxidised only with difficulty by alkaline permanganate. Its constitution is proved by the fact that it yields dicarbethoxyacetanilide (5) when heated at 100°, the identity of the latter being settled by a comparison with the condensation product of ethyl malonate and phenylcarbimide. On heating at higher temperatures (best 240—250°) 6-*anilino*-2 : 4-*diketo*-3-*phenyl*-2 : 4-*dihydro*-1 : 3-*oxazine*, m. p. 293—294°, is formed by the condensation of (5) with phenylcarbimide. *Ethyl* 2-p-*chlorophenyldimethylene*-1 : 2-*oxaimine*-4 : 4-*dicarboxylate*, m. p. 122—123°, and the corresponding p-*bromo* compound, m. p. 132—133°, were obtained similarly to (3) on using the *p*-halogen-substituted nitrosobenzenes. Staudinger and Jelagin (A., 1911, i, 215) obtained (7) and only traces of (8) by the addition of diphenylketen, $\overset{-}{O}C\overset{+}{:}\overset{-}{C}Ph_2$, to nitrosobenzene, (7), (8), whilst (8) would be expected from the polarity theory. Diphenylethylene (2) is a compound in which the polarities are oppositely directed with respect to the heavy substituent to those of (1). It may be represented by the polar formula, $\overset{-}{C}H_2\overset{+}{:}CPh_2$. According to the polar theory it should unite with $O\overset{+}{:}NPh$ to form (9) and not (10). Only (10) was formed. 2 : 3 : 3-*Triphenyldimethylene*-1 : 2-*oxaimine* (10), m. p. 218—220°, closely resembled the above dimethyleneoxaimines. On distillation at 70 mm., it decomposed, yielding benzophenonanil and formaldehyde. As an example of an ethylene derivative in which the *gem*-group is absent, styrene was allowed to react with nitrosobenzene. No dimethyleneoxaimine was formed, the product being a six-membered ring (11) which breaks

down into *N*-phenylbenzaldoxime, formaldehyde, and phenylhydroxylamine.



N-p-*Chlorophenylbenzaldoxime*, m. p. 172—173°, was obtained from styrene and *p*-chloronitrosobenzene. A. C.

Anhydrides of Amino-acids and their Derivatives. P. KARRER and C. GRÄNACHER (*Helv. Chim. Acta*, 1924, **7**, 763—780).—When 2 : 5-dihydroxydihydropyrazine dibenzyl ether (this vol., i, 212) and phthalic anhydride are heated together at 150—200°, glycine and benzylphthalic acid are formed, and when the pyrazine compound and methyl iodide are heated together at 100—120°, sarcosine anhydride and benzyl iodide are produced. The silver salt of glycine anhydride reacts with ethyl ω-chloro-*p*-toluate to give 2 : 5-*dihydroxydihydropyrazine di*-p-*carbethoxybenzyl ether*, m. p. 196—198°. The corresponding dicarboxylic *acid* melts and chars at 230—235°; it, like its congener (*loc. cit.*), is readily hydrolysed by dilute hydrochloric acid.

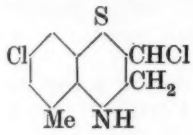
Ethyl hippurate is dehydrated when treated with phosphorus pentachloride (on the water-bath) yielding 5-*ethoxy*-2-*phenyloxazole*, b. p. 150—152°/12 mm. (*hydrochloride*, m. p. 115—120°; *picrate*, m. p. 122—123°). Warm, dilute hydrochloric acid readily decomposes this compound to ethyl alcohol and hippuric acid. Methyl acetamidoacetate, similarly dehydrated (in chloroform solution), yields 5-*ethoxy*-2-*methyloxazole*, b. p. 60—62°/10—12 mm. (*picrate*, m. p. 98°). The ethyl ester of benzoyl-*l*-leucine yields 5-*ethoxy*-2-*phenyl*-4-iso*butyloxazole*, b. p. 133—134°/2 mm. (*picrate*, m. p. 81°), and that of acetyl-leucine affords 5-*ethoxy*-2-*methyl*-4-iso*butyloxazole*, b. p. 87—89°/20 mm. (*picrate*, m. p. 80—81°). All these oxazoles are easily decomposed by dilute acid.

Hippuric anilide also is dehydrated by treatment with phosphorus pentachloride and thus affords 5-*chloro*-1 : 2-*diphenylglyoxaline*, m. p. 133° (*picrate*, m. p. 157—158°). The compound is stable towards hot hydrochloric acid; the chlorine atom also is firmly attached. 5-*Chloro*-2-*phenyl*-1-*ethylglyoxaline*, m. p. 65—67° (*picrate*, m. p. 160—161°), is obtained in a similar way from *hippuric ethylamide*, m. p. 147—148°. Hippuramide yields 5-*hydroxy*-2-*phenylglyoxaline*, m. p. 141—143°. This compound is decomposed by hot dilute hydrochloric acid.

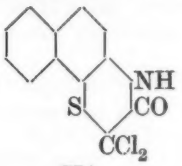
The relationship of the above investigations to the question of the structure of proteins is discussed. W. A. S.

Halogenated Ketodihydroaryl-*p*-thiazines. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (K. ZAHN) (D.R.-P. 379318; from *Chem. Zentr.*, 1924, i, 1104—1105).—The following compounds obtained by chlorination of ketodihydroaryl-*p*-thiazines in the methylene group of the thiazine ring are described: *Chloroketodihydrobenz*-p-*thiazine*, m. p. 212° (decomp.); *dichloroketodihydro-*

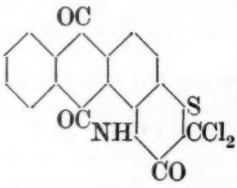
benz-p-*thiazine*, m. p. 185° (decomp.); *bromoketodihydrobenz*-p-*thiazine*; *dibromoketodihydrobenz*-p-*thiazine*; *chloroketodihydro*-5-*methyl*-7-*chlorobenz*-p-*thiazine* (I), m. p. 240°; 2-*dichloroketodihydro*-5-*methyl*-7-*chlorobenz*-p-*thiazine*, m. p. 205°; *monochloroketodihydronaphth*-p-*thiazine*, blackening at 210°; *dichloroketodihydronaphth*-p-*thiazine* (II), m. p. about 230° (decomp.); *dichloroketodihydroanthraquinonyl*-p-*thiazine* (III).



(I.)



(II.)



(III.)

G. W. R.

4-Nitro-2-sulphophenyldehydrothio-*p*-toluidinesulphonic Acid. D. H. Peacock (*J. Chem. Soc.*, 1924, **125**, 1547).—This compound was prepared by condensing sodium dehydrothio-*p*-toluidinesulphonate with sodium 6-chloro-3-nitrobenzenesulphonate. The *potassium* salt, $C_{20}H_{13}O_8N_3S_3K_2$, dyes cotton in bright yellow shades tinged with green. The *silver*, *lead*, and *barium* salts have been prepared. The potassium salt with strong alcoholic potassium hydroxide yields a bronze, crystalline powder which appears to contain the :NK group.

4-*Amino*-2-*sulphophenyldehydrothio*-p-*toluidinesulphonic acid*, obtained on reducing the nitro compound, dyes cotton very pale shades. The diazo compound couples on the fibre with β-naphthol to produce a bright rose, and with *m*-phenylenediamine a full brown shade. A. C.

Condensation of Aryldiazonium Salts and of Alkyl Nitrites with Derivatives of Cyanoacetic Acid. T. K. Walker (*J. Chem. Soc.*, 1924, **125**, 1622—1625; cf. T., 1923, **123**, 2775).—Difficulties in preparing benzylcyanoacetic ester were overcome (yield 60%) by use of excess of cyanoacetic ester (cf. A., 1893, i, 16; 1899, i, 897), and treatment with sodium hydroxide gave the acid. Ice-cold solutions of alkylcyanoacetic acids reacted with aryldiazonium salts according to the equation $CHR(CO_2H)\cdot CN + Ar\cdot N_2\cdot OH \longrightarrow CR(:N\cdot NHAr)\cdot CN + H_2O$ (where R=CH_2Ph, Ph, or Et); the following hydrazones were thus obtained: *phenylpyruvonitrilephenylhydrazone* (100% yield), m. p. 157°, converted by boiling alcoholic potassium hydroxide into *phenylpyruvic acid phenylhydrazone*, m. p. 161°; *phenylpyruvonitrile*-p-*tolylhydrazone* (yield 25%), m. p. 113°; *phenylpyruvonitrile*-p-*nitrophenylhydrazone* (small yield), m. p. 167—168°; *methylpyruvonitrile*-p-*tolylhydrazone*, m. p. 143—144°; *methylpyruvonitrile*-p-*chlorophenylhydrazone*, m. p. 172°; *phenylglyoxylonitrilephenylhydrazone*, m. p. 152°.

Nitrous acid and alkyl nitrites were without action on monoalkylcyanoacetic acids, whilst the esters only yielded oximino derivatives, CN·CR:NOH, when treated with potassium ethoxide

at 0° in dry ethereal solution. Thus ethyl benzylcyanoacetate reacted with amyl nitrite; cautious acidification yielded *phenylpyruvonitrile oxime*, an unstable red oil (*silver* salt described). Its constitution was established by hydrolysing with acid to hydroxylamine, whilst heating with alcoholic potassium hydroxide gave α-oximino-β-phenylpropionic acid. Similarly, from ethyl ethylcyanoacetate there was prepared *methylpyruvonitrile oxime*, a red oil (*potassium*, *sodium*, and *silver* salts described); ethyl phenylcyanoacetate gave *phenylglyoxylonitrile oxime* (small yield), m. p. 129°.

The general conclusion from these and previous results is that an aryldiazonium salt condenses with a compound CHRXY (where X=CO_2H, CO_2R', COR', CN and Y=CO_2H, CO_2R'); alkyl nitrites condense similarly except when, simultaneously, X=CN and Y=CO_2H. Nitrosobenzene does not react with CHRXY, although it usually condenses readily with CH_2XY. F. M. H.

Preparation of Aminoazo Compounds. FARBENFABR. VORM. F. BAYER U. CO. (J. HALLER) (D.R.-P. 381916; from *Chem. Zentr.*, 1924, i, 1592).—Negatively substituted *o*-aminodialkylanilines are diazotised and the diazo compounds coupled with diazotisable amines. Compounds are thus prepared from diazotised 4-nitro-2-amino-1-dimethylaniline or 2-amino-4-methoxytoluene and *p*-xylidine, from diazotised 4-chloro-2-amino-1-dimethylaniline and 2-amino-4-methoxytoluene, and finally from diazotised 4-nitro-2-amino-*N*-methyldiphenylamine and *m*-aminoacetanilide. 4-*Nitro*-2-*amino*-N-*methyldiphenylamine* has m. p. 69—70°. G. W. R.

Halogen-substituted Aromatic Hydrazines. II. 2 : 3-, 2 : 5-, 2 : 6-, and 3 : 5-Dibromophenylhydrazines and *p*-Bromophenylmethylhydrazine and their Reaction Products with Aldehydes and Ketones. E. VOTOČEK and R. LUKES (*Bull. Soc. chim.*, 1924, [iv], **35**, 868—879).—Of the above hydrazines, only the 2 : 5- and 3 : 5-dibromophenylhydrazines have been previously prepared. The 2 : 5-*dibromophenylhydrazones* of the following are described: *acetone*, m. p. 93°; *benzaldehyde*, m. p. 79°; *furfuraldehyde*, m. p. 104°; *arabinose*, m. p. 170—175°; *galactose*, m. p. 207°; *rhamnose*, m. p. 184°; *glucose* 2 : 5-*dibromophenylosazone*, m. p. 228—229°. The corresponding osazone of galactose could not be prepared in a pure state.

3 : 5-*Dibromophenylhydrazones* of the following are described: *acetone*, m. p. 85—86°; *benzaldehyde*, m. p. 106—107°; *furfuraldehyde*, m. p. 116°; *glucose*, m. p. 158—159°; *rhamnose*, m. p. 195—196°; *galactose*, m. p. 172°. The corresponding osazones of dextrose and galactose were isolated in an impure state.

2 : 3-*Dibromophenylhydrazine*, m. p. 112°, was prepared from 2 : 3-dibromoaniline by diazotisation and subsequent reduction with stannous chloride. *Acetone* 2 : 3-*dibromophenylhydrazone*, *benzaldehyde* 2 : 3-*dibromophenylhydrazone*, m. p. 106°, and the corresponding *osazones* of dextrose and galactose, which are both difficult to purify, are described.

2 : 6-*Dibromophenylhydrazine*, m. p. 110°, was similarly obtained

from 2 : 6-dibromoaniline. *Acetone* 2 : 6-*dibromophenylhydrazone* (oil), *benzaldehyde* 2 : 6-*dibromophenylhydrazone*, m. p. 51—52°, unstable, and *furfuraldehyde* 2 : 6-*dibromophenylhydrazone*, m. p. 62°, are described. This hydrazine forms no characteristic hydrazones or osazones with the sugars.

as.-p-*Bromophenylmethylhydrazine*, m. p. 33°, was obtained by bromination of phenylmethylhydrazine in cold concentrated hydrochloric acid solution. *Benzaldehyde* p-*bromophenylmethylhydrazone*, m. p. 106—107°, *acetone* p-*bromophenylmethylhydrazone*, an unstable oil, and *lævulose* p-*bromophenylmethylosazone*, m. p. 153°, are described.

It is proved by two methods that bromination of phenylmethylhydrazine under the above conditions leads to a *p*-bromo derivative. Methylation of *p*-bromoaniline followed by the formation and reduction of the corresponding nitrosoamine gives *p*-bromophenylmethylhydrazine identical with the compound produced by direct bromination of phenylmethylhydrazine. *p*-Bromophenylmethylhydrazine was also reduced to *p*-bromomethylaniline, giving a nitroso compound identical with that produced by the first method. In the bromination of phenylmethylhydrazine no *o*-bromophenylmethylhydrazine can be detected. A. E. C.

Formation of Triphenylmethylphosphinic Acid from Triphenylmethoxyphosphorus Dichloride. D. R. Boyd and F. J. Smith (*J. Chem. Soc.*, 1924, **125**, 1477—1480).—Alcoholic potassium hydroxide converts triphenylmethylphosphorus dichloride into an acid, which was assumed by Boyd and Chignell (T., 1923, **123**, 813) to have the formula $CPh_3{\cdot}O{\cdot}P(OH)_2$. Alkylphosphorous acids of this type are monobasic, but if the above acid dissolved in one equivalent of sodium hydroxide is titrated with more alkali, the curve showing the change of p_H with increase of alkali concentration indicates the presence of a second salt. The alternative formula, $CPh_3{\cdot}PO(OH)_2$, is more in harmony with the dibasic character of the acid. The latter forms triphenylmethane when heated with soda-lime, a reaction characteristic of phosphinic acids. There is evidently a molecular rearrangement during which tervalent phosphorus becomes quinquevalent. (1) $CPh_3{\cdot}O{\cdot}PCl_2 \rightarrow CPh_3{\cdot}PO(OEt){\cdot}OK$.

In the case of the reaction between phosphorus trichloride and triphenylcarbinol, the reaction proceeds according to equation (2) to the extent of 78% of the carbinol employed (the normal reaction between phosphorus trichloride and an alcohol; Menschutkin, 1866) whilst about 5% of the carbinol appears to react according to (3): (2) $R{\cdot}OH+PCl_3=PHCl_3{\cdot}OR=PCl_2{\cdot}OR+HCl$. (3) $R{\cdot}OH+PCl_3=PHCl_3{\cdot}OR=PCl_2R{:}O+HCl$. Reaction (3) will tend to take place where the alcohol is pronouncedly basic with a tendency to dissociate into R· and ·OH. It is important to notice that $CPh_3{\cdot}O{\cdot}PCl_2$ is specially stable towards water whilst compounds of the type $R{\cdot}O{\cdot}PCl_2$ are usually readily hydrolysed by water. It is suggested that alcohol is first added on to the unsaturated phosphorus atom, then, under the influence of the hot alcoholic potassium hydroxide

the disturbance of the molecule due to this and to the splitting off of hydrogen chloride may produce a state favourable to the migration of the triphenylmethyl group from oxygen to phosphorus as in (1) above. Directions are given for improving the yield of triphenylmethylphosphorus dichloride. Triphenylmethylphosphinic acid prepared as previously described was found to contain about 50% of its monoethyl ester; the pure acid has m. p. 275°. The yield was increased to 80% of theory by using 5—6 mols. of potassium hydroxide (in place of 3). *Dipotassium triphenylmethylphosphinate* ($+3H_2O$) and *barium triphenylmethylphosphinate*,

$$CPh_3 \cdot PO_3Ba,4H_2O,$$

are described. A. C.

Chemistry of the Blood Colouring Matter. II. Chemical Character of Kathæmoglobin. F. HAUROWITZ (*Z. physiol. Chem.*, 1924, **137**, 62—77).—Mainly from spectroscopic and magnetic investigations of kathæmoglobin, the latter is shown to behave as if it were a Zsigmondy "colloid-compound" of hæmatin and globin. α-Hæmin (and from this, crystalline chlorohæmin) was obtained by digesting kathæmoglobin with pepsin and hydrochloric acid. B. F.

Products of the Catalytic Hydrolysis of Goose Feathers. W. S. SSADIKOV and N. D. ZELINSKY (*Biochem. Z.*, 1924, **147**, 30—69).—A highly detailed experimental account of the application to goose feathers of the authors' catalytic method of fragmenting proteins of which a preliminary announcement has already been made (A., 1923, i, 492). The isolation of many substances of the type of peptin and piprin anhydrides is described and the results of analyses are detailed. Such complex cyclic compounds are regarded as precursors of the amino-acids obtained on ultimate hydrolysis, the peptins giving rise to peptides as intermediates, and the piprins to piperidones. Many other complex derivatives, several of which are described, formed by secondary changes of the real protein units, may arise in the course of catalytic hydrolysis of ring structures. J. P.

Biochemistry.

Pharmacology of Cell Respiration. V. Influence of γ-Rays on Cell Respiration. F. HAZAMA (*Z. physiol. Chem.*, 1924, **138**, 102—107).—Small doses of γ-rays usually cause a transitory increase in the oxygen consumption of the erythrocytes of the goose, provided that at least 4 hours have elapsed since the removal of the erythrocytes from the body; large doses are without effect. E. S.

Chondroitinsulphuric Acid in Serum. K. DRESEL (*Klin. Woch.*, 1923, **2**, 2344—2345; from *Chem. Zentr.*, 1924, i, 1554—1555).—Chondroitinsulphuric acid, normally excreted in the urine, may be retained in certain pathological conditions. G. W. R.

Adsorption of Sodium Salicylate by Blood-serum. R. COQUOIN (*Compt. rend. Soc. Biol.*, 1923, **89**, 1259—1261; from *Chem. Zentr.*, 1924, i, 1558).—On long-continued dialysis an equilibrium is established with respect to salicylate between serum and a physiological salt solution. No adsorption of sodium salicylate by serum takes place. This is contrary to the view of Chabanier, Lebert, and Lobo-Onell (*Compt. rend. Soc. Biol.*, 1923, **88**, 178). G. W. R.

Serum Proteins. (Method of Obtaining Serum and Criticism of Rohrer's Method of Determining the Albumin–Globulin Value.) W. VON FREY (*Biochem. Z.*, 1924, **148**, 53—60). —The differences between plasma-serum and ordinary blood-serum (from a clot) are not evident if alterations of carbon dioxide tension are prevented by keeping the preparations under a layer of paraffin (cf. Leendertz, *Arch. klin. Med.*, 1922, **140**). Refractometric methods of determining serum proteins do not give trustworthy results, these being in general higher than those obtained by chemical methods. The Hammarsten and Rohrer methods of determining the albumin–globulin value do not give concordant results, a finding which is ascribed to the untrustworthiness of the latter method. J. P.

Effect of Exercise on Sugar and Residual Nitrogen in Blood. CÄSAR and SCHAAL (*Z. klin. Med.*, 1924, **98**, 96—99; from *Chem. Zentr.*, 1924, i, 1553).—The blood-sugar was more than doubled after a foot race. The effect is reached 20—46 minutes after the event. No marked effect on the residual nitrogen of the blood was noted. G. W. R.

Changes in Blood-sugar. I. S. NAKAHAYASHI and J. ABELIN (*Biochem. Z.*, 1924, **147**, 544—556).—From determinations of the polarimetric and copper-reducing values (Bertrand) of deproteinised aqueous blood filtrates the authors claim to substantiate the results of Winter and Smith (*J. Physiol.*, 1922, **57**, 100). Although the figures published show a general tendency of the polarimeter value to rise, this is irregular and falls are sometimes recorded. In four normal cases (sheep's blood), the initial polarimeter value instead of being below the copper-reducing value, as the authors state, is above the latter or insignificantly below it. The feeding of thyroid material does not influence the behaviour of the blood filtrate, but after adrenaline injections this shows a polarimeter value above that of the copper-reducing value—exceptions again occur—and the general tendency is for the former to fall. Some days after the adrenaline injection the blood filtrates again show "normal" behaviour. J. P.

Distribution of Blood-sugar between Corpuscles and Plasma. F. Högler and K. Ueberrack (*Biochem. Z.*, 1924, **148**, 150—159).—In the rabbit, the ratio of corpuscle sugar to plasma sugar is very small. In human plasma, from blood to which anti-coagulant has been added in deficient amount, the blood-sugar results are too low. Hæmolysis leads to high results. Using sufficient anti-coagulant and avoiding hæmolysis, plasma and sera prepared by various methods give concordant blood-sugar results. Human corpuscles contain 50—80 mg. % of sugar. J. P.

Determination of Blood-sugar. L. Pincussen and N. Klissiunis (*Biochem. Z.*, 1924, **150**, 44—48).—Comparative determinations of blood-sugar from different parts of the circulation show that higher values may sometimes be obtained in blood from the right hand than in blood from the left, and in blood from either hand than in that from the lobe of the ear. It is suggested that blood obtained by capillary puncture (as from the ear) must always be diluted with tissue fluids; also that the blood is richer in sugar when circulating through active parts. The latter assumption is supported by the observation that the blood of a paralysed limb always contains less sugar than blood from other parts of the same individual's body. C. R. H.

Blood-sugar of Rabbits under Various Conditions. N. Mochizuki (*Biochem. Z.*, 1924, **150**, 123—143).—Ligature of the pancreatic duct produces a gradually increasing degree of hyperglycæmia in rabbits; animals thus treated show a greater hyperglycæmia after feeding with dextrose and after injection of adrenaline than do normals; during the first 10 days after operation an increased proportion of the total blood-sugar is contained in the corpuscles. The slight rise in blood-sugar which follows administration of pilocarpine and of phloridzin in normal animals is replaced by a fall in the operated animals in the case of the latter substance, whilst in the case of the former no effect at all is observed. C. R. H.

Action of Uranyl Acetate. III. Action on Red Blood-corpuscles. III. Y. Mikawa (*Biochem. Z.*, 1924, **149**, 550—555).—Uranyl acetate agglutinates the red corpuscles of rabbit blood without hæmolysing them. Such agglutinated corpuscles are not hæmolysed by saponin. This is probably due to a fixation of the hæmoglobin by the uranyl acetate. Small amounts of this salt damage the structure of the cells, as is shown by their increased sensitiveness to physiological saline solution. S. S. Z.

Partition of Chlorides between Plasma and Corpuscles in Human Blood. F. Högler and K. Ueberrack (*Biochem. Z.*, 1924, **150**, 18—22).—No difference could be detected between the chlorine content of serum and of plasma; the ratio of corpuscle-chlorine to plasma-chlorine is approximately constant both in normal individuals and in those suffering from nephritis, and is of the same magnitude as the ratio of the sugar of the corpuscles to the sugar of the plasma. C. R. H.

Changes in Chlorine Content of Whole Blood and Blood-serum of Infants in Relation to Gastric Secretion. W. SCHOBER (*Monatschr. Kinderheilk.*, 1923, **26**, 297—307; from *Chem. Zentr.*, 1924, i, 1948).—The chlorine content of the serum of suckling infants falls 2 hours after feeding, rising again after 3 hours. The chlorine content of the whole blood generally increases after feeding. The chlorine in the hydrochloric acid of gastric juice is not supplied entirely by the blood, but must come, in part, from chlorine reserves in the tissues. G. W. R.

Action of Intravenous Infusions of Sodium Chloride and Sugar on the Alkali Reserve of the Blood. Y. FUJIMAKI (*Arch. exp. Path. Pharm.*, 1924, **103**, 178—187).—One and a half hours after the injection of sodium chloride and sugar into the rabbit a rise in temperature is produced which is associated with diminished lung ventilation and a resulting retention of carbon dioxide. This is in turn compensated by an increase in the alkali reserve. J. P.

Acid–Base Equilibrium of the Blood of Normal Guinea Pigs, Rabbits, and Rats. J. A. HAWKINS (*J. Biol. Chem.*, 1924, **61**, 147—155).—Guinea pigs and rabbits, which show large variations in body temperature, show also variations in the acid–base equilibrium of their blood; rats, on the other hand, both in body temperature and in acid–base equilibrium, are relatively stable. C. R. H.

Effect of Methylamine Hydrochloride and Ammonium Chloride on the Physiological Osmotic Pressure of Sodium Chloride Solutions. M. DUVAL (*Compt. rend. Soc. Biol.*, 1923, **89**, 1268—1270; from *Chem. Zentr.*, 1924, i, 1558).—With rabbit blood-corpuscles methylamine hydrochloride and ammonium chloride behave like acetamide (Duval, *Compt. rend. Soc. Biol.*, 1923, **88**, 1196). In solutions poor in sodium chloride but rich in methylamine, hæmolysis occurs. Hæmolysis is due to the lowering of the physiological osmotic pressure of the solution against that of the blood-corpuscles. G. W. R.

Non-coagulable Nitrogen of Blood, and Muscular Work. G. AIELLO (*Rif. med.*, 1923, **39**, 721—722; from *Chem. Zentr.*, 1924, i, 1945).—Muscular work, involving protein decomposition and increase in blood concentration, resulted in an increase in the residual nitrogen of the blood. No relationship was observed between blood pressure and residual nitrogen. G. W. R.

Globulin and Albumin Coefficients of Serum especially during Pregnancy. H. KÜRTEN (*Arch. exp. Path. Pharm.*, 1924, **103**, 237—238).—A citation of the author's previous work (*Biochem. Z.*, 1922, **133**, 126; 1923, **135**, 536) in relation to that of Hafner (*Arch. exp. Path. Pharm.*, 1924, **101**, 336). J. P.

Investigations of the Blood of Individual Animals. III. W. KÜSTER (*Z. physiol. Chem.*, 1924, **138**, 21—37).—The preparation and alkylation of hæmins from the blood of different animals

are recorded. The results indicate that the crude hæmin consists of a mixture and suggest that various hæmoglobins occur in one and the same blood. E. S.

Formation of Porphyrin from "Carbon Dioxide Blood." P. LIST (*Z. physiol. Chem.*, 1924, **138**, 164—170; cf. *ibid.*, 1924, **135**, 95).—From blood which has been saturated with carbon dioxide and subsequently treated with 25% hydrochloric acid there was obtained a substance of the nature of porphyrin which could be further separated into two components, one of which could be extracted from hydrochloric acid solution with chloroform whilst the other could not. Both components could be extracted together by means of ether after neutralising the solution and acidifying with acetic acid. Details are given of spectroscopic observations on the mixture and the two components separately. C. R. H.

Ammonia Content of Blood. V. HENRIQUES and E. GOTTLIEB (*Z. physiol. Chem.*, 1924, **138**, 254—261).—A series of experiments on the amounts of ammonia recoverable from blood by prolonged aëration leads to the conclusion that the circulating blood contains no preformed ammonia, and that any which may be found is the product of *in vitro* reactions in the drawn blood. C. R. H.

Distribution of Carbamide in Blood and in Cerebrospinal Fluid. M. POLONOVSKI and C. AUGUSTE (*J. Physiol. pathol. gén.*, 1923, **21**, 267—282; from *Chem. Zentr.*, 1924, i, 1945—1946).—Plasma and serum have the same content of carbamide, but the erythrocytes contain 5 to 8% less. For every type of blood there is a characteristic distribution of carbamide, which is quickly restored if a part of the plasma is replaced by sodium chloride solution or by concentrated carbamide solution. Cerebrospinal fluid contains from 1 to 25% less carbamide than peripheral venous blood. G. W. R.

Fats and Lipoids in Blood. I. Distribution of Cholesterol and other Lipoids in the Blood of Different Animals. R. IWATSURU (*Pflüger's Archiv*, 1924, **202**, 194—199; from *Chem. Zentr.*, 1924, i, 1947).—The cholesterol, fat, and lipoid content is practically constant in the corpuscles of various mammals. The values obtained were 215 mg. of cholesterol, and 580 mg. of fats and lipoids (calculated as triolein) per 100 c.c. of blood. Variations of these substances in the whole blood of various species and individuals are due to differences in the amounts appearing in the plasma. G. W. R.

New Basic Crystalline Constituent of Blood. I. A. LEIMDÖRFER (*Biochem. Z.*, 1924, **149**, 513—524).—A new basic substance is described which can be obtained from the blood-corpuscles of human and mammalian blood by boiling with dilute acetic acid, extracting with alcohol, and precipitating with alcoholic cadmium chloride. It is present in the erythrocytes only. It gives a diazo reaction when sodium or potassium hydroxide is

employed but not when ammonia or sodium carbonate is used. It is obtained from the cadmium compound by removing the metal with hydrogen sulphide, dissolving in alcohol, and precipitating with ether. It can also be precipitated directly from the alcoholic extract of the corpuscles with ether. The substance has not yet been prepared in a pure condition; the analyses suggest so far that it contains N, C, and H in the approximate proportions 1 : 3–5 : 7–9. S. S. Z.

Transformation of Blood Pigment into Bile Pigment. T. Brugsch and E. Pollak (*Biochem. Z.*, 1924, **147**, 253—254).—It is claimed that by the action of pyrocatechol, hæmin and its derivatives are converted into bile pigment (bilirubin). Quinol and resorcinol do not act in this way. J. P.

Blood Pigments. III. Methæmoglobin and its Derivatives. F. Haurowitz (*Z. physiol. Chem.*, 1924, **138**, 68—99).—Both colorimetric and spectroscopic methods show that methæmoglobin exists in two forms in aqueous solution. When the reaction of the medium is more alkaline than p_H 10·0 it is present entirely as alkaline methæmoglobin, and when more acid than p_H 6·0 entirely as acid methæmoglobin; between these hydrogen-ion concentrations equilibrium mixtures exist.

Pure, crystalline methæmoglobin is best prepared by allowing pure oxyhæmoglobin to stand for 6—8 weeks in 20% alcohol in the presence of air; its formation by means of other reagents has been studied. The action of nitrite on oxyhæmoglobin results in the formation of a mixture of nitric oxide–hæmoglobin and methæmoglobin and not, as stated by Hartridge (A., 1921, i, 135), of nitrite-hæmoglobin. Pure fluormethæmoglobin has been found to contain one atom of fluorine to one of iron. E. S.

Mechanism of Hæmolysis in Hypertonic Salt Solutions. D. Acél and L. Lorber (*Biochem. Z.*, 1924, **147**, 557—562).—Strongly hypertonic salt solutions (5—50%), except those with physiologically inactive anions (citrate, sulphate), hæmolyse red blood-corpuscles. The order of activity of the anions for salts with the same cation conforms to the Hofmeister series. In the salts of multivalent metals the activity of the cation is important. The process is regarded as being similar to hypotonic hæmolysis and support is thereby gained for the view that the erythrocyte is a colloidal structure containing hæmoglobin in its interstices, and not a closed semi-permeable membrane filled with the pigment. In weakly hypertonic solutions osmosis predominates, whilst in stronger salt solutions the imbibition of water by the colloid substance of the cells begins to play a part. J. P.

Influence of Sunlight on Protein Metabolism. L. Pincussen (*Biochem. Z.*, 1924, **150**, 36—43).—Irradiation causes an increase in the general metabolism of rabbits, as shown by an increase in nitrogenous excretion, which is increased by the use of sensitisers, such as various dyestuffs and potassium iodide. Differences in the action of the various sensitisers may be observed

in their effect on individual constituents of the total excreted nitrogen. C. R. H.

Nitrogen Metabolism in Avitaminosis. S. Yoshiue (*Biochem. Z.*, 1924, **148**, 1—48).—In avitaminosed dogs, a diminution in intestinal absorption leads to a lessened urea formation and an increased excretion of amino-nitrogen and ammonia, a disturbance which can be reduced in intensity by any condition bringing about increased absorption. This condition of acidosis may appear at all stages of avitaminosis and is often apparently of a temporary nature and not directly associated with the latter, whilst at other times it is due to a progressive deterioration in the condition of the gastro-intestinal tract. An increase in protein metabolism, leading ultimately to a breakdown of cell proteins, is a primary result of avitaminosis. The rapidity with which the effects of avitaminosis become manifest is much greater in young than in old animals, varying more or less inversely with the age. J. P.

Pancreas and Carbohydrate Balance. E. Toenniessen (*Klin. Woch.*, 1924, **3**, 212—213; from *Chem. Zentr.*, 1924, i, 1557). —It is held that the pancreas does not take part in the catabolism of carbohydrates to lactic acid, but is concerned only in the later stages of degradation. G. W. R.

Lactic Acid Formation in Muscular Contraction. O. Meyerhof, H. E. Himwich, and Matsuoka (*Klin. Woch.*, 1924, **3**, 392—395; from *Chem. Zentr.*, 1924, i, 2174).—Contraction of isolated muscle caused by chloroform, caffeine, or heat is accompanied by the formation of lactic acid and is analogous in this respect to natural or electrically produced contraction. Contraction due to acetylcholine is not accompanied by lactic acid formation. Chloroform contraction can be inhibited by novocaine. G. W. R.

Muscular Exercise, Lactic Acid, and the Supply and Utilisation of Oxygen. I—III. A. V. Hill, C. H. N. Long, and H. Lupton (*Proc. Roy. Soc.*, 1924, **B**, **96**, 438—475).—I. *Introduction.* Previous work (A., 1923, ii, 977) and the various aspects of the problem as presented in skeletal and heart muscle, are discussed.

II. *Determination of lactic acid in biological fluids.*—Clausen's permanganate method (A., 1922, ii, 593) with slight modifications is considered suitable for blood and urine. In blood to which zinc lactate has been added about 85% of the lactic acid is found by this method. Resting human blood contains 10 to 20 mg.% and urine 3 to 14 mg.%. Oxidation with 50% sulphuric acid at 140° as described by Clausen (*loc. cit.*) does not give good results and even with 60% acid at 155° only 80% of the lactic acid is accounted for.

III. *Lactic acid in blood and the respiratory quotient.*—During steady, moderate exercise the variations in both respiratory quotient and total lactic acid of the blood are small. During and for a short time after severe exercise the lactic acid concentration in-

creases to a maximum. The value then falls, owing to the diffusion of lactate ions into the blood stream and oxidative recovery. In blood to which lithium lactate has been added, the plasma attains a concentration of lactic acid about 50% higher than that of the blood as a whole, and in human blood after muscular exercise about 30% higher. The concentration in the corpuscles is considerably less than that in the plasma. The variations in the lactic acid concentration of muscle during exercise and in recovery lead to wide variations in the respiratory quotient. This increases with increase in vigour of the exercise and may reach the value of 2. It then falls to low values for a considerable period before returning finally to a normal resting value. All these changes depend merely on the liberation of lactic acid and its removal in recovery. O. O.

Degradation of Carbohydrates in Striped Muscle. IV. Biochemistry of α- and β-Glucose. F. Laquer and K. Griebel (*Z. physiol. Chem.*, 1924, **138**, 148—155).—The formation of lactic acid by a suspension of chopped muscle, already known (A., 1922, i, 1089; 1923, i, 268) to be increased by the addition of glycogen, is increased more by α-glucose than by β-glucose, the effect of ordinary dextrose being intermediate. In view of this it is suggested that α-glucose may be the particular form in which carbohydrate is actively metabolised in the organism. C. R. H.

Calcium Content of Normal and Diseased Skin. Gans (*Arch. Dermat. Syphilis*, 1924, **145**, 135—137; from *Chem. Zentr.*, 1924, i, 2162).—In normal skin, calcium occurs in the cutis, in rather less amount in the papillary bodies, with practically none in the epidermis. Changes in distribution occur in pathological conditions. In eczema, the calcium content of the epidermis greatly exceeds that of the papillary bodies and the cutis. A similar change is shown in the potassium content, principally on account of the exudative processes involved. G. W. R.

Retention of Lime by Animal Tissues. II. R. E. Liesegang (*Biochem. Z.*, 1924, **149**, 605).—Polemical. S. S. Z.

Calcium Fixation in the Development of Bone. E. Freudenberg and P. György (*Ergeb. inn. Med. Kindersheilk.*, 1923, **24**, 17—28; from *Chem. Zentr.*, 1924, i, 1952; cf. A., 1922, i, 608).—The physiological fixation of lime takes place in three stages which may be represented as follows: (1) cartilage protein + Ca=Ca–cartilage protein; (2) Ca–cartilage protein+phosphate= Ca–cartilage protein–phosphate; (3) Ca–cartilage protein–phosphate = calcium phosphate + cartilage protein. G. W. R.

Natural Porphyrins. VII. Urinoporphyrinogen Heptamethyl Ester and a New Conversion of Urino- into Coproporphyrin. H. Fischer and W. Zerweck (*Z. physiol. Chem.*, 1924, **137**, 242—264).—The two main porphyrins present in porphyrinuria, urino- and copro-porphyrin, have been separated by means of hot glacial acetic acid in which coproporphyrin is readily

soluble whilst urinoporphyrin is practically insoluble. Further, by esterifying with methyl sulphate a new *porphyrin* has been isolated. The crystalline *methyl* ester has m. p. 255—257°. The new porphyrin forms a crystalline *copper* salt, m. p. 292°. On hydrogenating urinoporphyrin methyl ester in the presence of platinum, it takes up 4 atoms of hydrogen, and yields the leuco compound, $C_{47}H_{54}O_{16}N_4$ (colourless prisms, m. p. 148°). It is easily reconverted into urinoporphyrin by atmospheric oxidation. Urinoporphyrin, on oxidation with chromic acid, gives an inactive, crystalline carboxylated hæmatic acid. On reduction with hydriodic acid and phosphorus iodide, it yields a pyrrole acid giving an intense Ehrlich reaction. When the reduction is carried out in the cold ammonia is formed to the extent of one-third of the total pyrrole nitrogen. This is in harmony with the assumption that urinoporphyrin contains two hydroxypyrrole nuclei. The conversion of urinoporphyrin into coproporphyrin (A., 1916, i, 775) has been effected by heating it with 1% hydrochloric acid for 3 hours at 180—185°. D. R. N.

Natural Porphyrins. VIII. Occurrence of Urinoporphyrin (as Copper Salt, Turacin) in Turakoo Birds and the Demonstration of Coproporphyrin in Yeast. H. Fischer and J. Hilger (*Z. physiol. Chem.*, 1924, **138**, 49—67).—The identity of turacin (A., 1923, i, 964) with the copper salt of urinoporphyrin has been confirmed by a comparison of the two salts; moreover, removal of the metal from turacin by reduction with sodium amalgam and subsequent oxidation in the air yields urinoporphyrin.

When the copper salts of coproporphyrin and urinoporphyrin are submitted to dry distillation, the products, which in each case consist of a new copper salt, have been shown by crystallographic and spectroscopic examination to be identical. That a relationship exists between coproporphyrin and urinoporphyrin is thus established.

Coproporphyrin, identified as its crystalline ester, has been isolated from putrefying yeast. This is the first occasion on which an animal porphyrin has been isolated from plant material. E. S.

Natural Porphyrins. IX. Ooporphyrin from Plovers' Egg Shells and its Relationship to Blood Pigments. H. Fischer and F. Kögl (*Z. physiol. Chem.*, 1924, **138**, 262—275).—The authors have isolated from plovers' egg shells a methyl ester which proves to be identical with the ooporphyrin dimethyl ester previously obtained from gulls' egg shells (this vol., i, 230). On boiling for 1 minute with a mixture of glacial acetic acid and hydriodic acid, this ester gives mesoporphyrin; with glacial acetic and hydrobromic acids it gives hæmatoporphyrin. These two reactions show that ooporphyrin belongs to the hæmoglobin group of pigments. The identity of ooporphyrin with Kämmerer's porphyrin and with the porphyrin obtained by Papendieck (this vol., i, 894) from blood treated with hydrogen sulphide, has been proved by the fact that the latter also undergo the two reactions mentioned above, and further by the identity of the complex

salts with iron ("hæmin esters") prepared from the dimethyl esters of all three porphyrins. C. R. H.

Natural Porphyrins. X. Blood Pigments in Yeast. Detection of Porphyrin in Plants. H. FISCHER and J. HILGER (*Z. physiol. Chem.*, 1924, **138**, 288—306).—In the autolysis of yeast there was obtained, besides the coproporphyrin already described (this vol., i, 894) as resulting from the bacterial putrefaction of yeast, Kämmerer's porphyrin, which was identified spectroscopically; after removing the porphyrin with 5% hydrochloric acid the solution of the remaining products of autolysis gave the hæmin spectrum, and on evaporation to dryness and treatment with pyridine, a definite hæmochromogen spectrum. The latter result was also obtained after plasmolysis of the yeast with ether and glacial acetic acid. Kämmerer's porphyrin was also obtained when blood was added to a fermenting mixture of sucrose and yeast, and after fermentation had ceased the whole was submitted to autolysis. Kämmerer's porphyrin was found in a sample of brewer's wort; coproporphyrin (probably) in hops. The spectra of porphyrins (unidentified) were obtained not only from grasses, by treating an alcoholic extract with glacial acetic acid, but also from chlorophyll-free coconut milk. C. R. H.

[**Spectroscopic Chemical Reactions of Porphyrins and their Derivatives.**] H. FISCHER (*Z. physiol. Chem.*, 1924, **138**, 307—313).—Polemical; reply to criticisms by Papendieck and Schumm (this vol., i, 460, 893) of the author's position with regard to the value of the spectroscopic method of analysis. C. R. H.

Compounds Extracted from Human Skeletal Muscle. Reply to J. A. Smorodinzev. R. ENGELAND and W. BIEHLER (*Z. physiol. Chem.*, 1924, **138**, 118).—Polemical (cf. this vol., i, 456). E. S.

Chemical Composition of Cardiac Muscle in Different Diseases. G. DOMAGK (*Z. klin. Med.*, 1924, **98**, 171—219; from *Chem. Zentr.*, 1924, i, 1551—1552).—Observations are recorded of the effect of certain pathological conditions on the content of non-protein nitrogen, fat, and water in cardiac muscle. G. W. R.

Metabolism of the Heart. I. Carbohydrate Balance of the Heart. P. SCHENK (*Pflüger's Archiv*, 1924, **202**, 315—328; from *Chem. Zentr.*, 1924, i, 2173).—The glycogen content of dogs' hearts is fairly constant. At any instant the content of carbohydrates intermediate between glycogen and lactic acid and including glucose and sugars of equal reducing power, forms a fairly constant proportion, approximately one-fifth, of the total carbohydrate present. The amount of lactic acid is extremely small and is probably due to the manipulations involved. It is improbable that lactic acid is a normal constituent of the resting muscle of warm-blooded animals. G. W. R.

Metabolism of the Heart. II. The Phosphoric Acid Balance of the Heart. P. SCHENK (*Pflüger's Archiv*, 1924, **202**, 329—336; from *Chem. Zentr.*, 1924, i, 2173; cf. preceding abstract).—The total phosphoric acid and lactacidogen phosphoric acid contents of heart muscle are appreciably higher than those of skeletal muscle. G. W. R.

Metabolism of the Heart. III. Carbohydrate and Phosphoric Acid Balance of the Heart after Injury. P. SCHENK (*Pflüger's Archiv*, 1924, **202**, 337—355; from *Chem. Zentr.*, 1924, i, 2173—2174; cf. preceding abstracts).—Data are given as to the effect of narcosis, hydrocyanic acid poisoning, and electrical stimulation on the carbohydrate and phosphoric acid balance in heart muscle. G. W. R.

Sulphuric Acid Content of Body Fluids in Normal and Pathological Conditions. R. MEYER-BISCH (*Biochem. Z.*, 1924, **150**, 23—35).—The concentration of total sulphuric acid in the blood-serum of normal individuals is about 18 mg. %. This amount is altered to a variable extent in nephritis and constantly raised in diabetes. The sulphuric acid content of the cerebrospinal fluid is greater than that of the serum, and is raised in meningitis, syphilis of the central nervous system, and encephalitis. Pleural exudates and œdema fluids contain about the same amount of sulphuric acid as the blood serum; lymph from the thoracic duct contains a variable amount but greater than the blood. C. R. H.

Solubility of Uric Acid. I. K. HARPUDER and H. ERBSEN (*Biochem. Z.*, 1924, **148**, 344—354).—In phosphate buffers uric acid is partly converted into urate, the amount of free uric acid in solution being independent of the hydrogen-ion concentration and practically constant about the true solubility value, whilst the proportion of urate depends on this constant concentration of free uric acid and on the hydrogen-ion concentration. The limiting degree of supersaturation of uric acid is partly dependent on the nature of the buffer acid present. J. P.

Solubility of Uric Acid. II. K. HARPUDER (*Biochem. Z.*, 1924, **148**, 355—369).—The behaviour of a supersaturated monourate solution at a p_H greater than 6·7 is ascribed to the presence of both undissociated uric acid and diurate, whilst in acid acetate and lactate buffers a supersaturation of undissociated uric acid is inferred. Non-electrolytes (dextrose, urea, glycine) and colloids (glycogen, globulin) increase the range of solubility of uric acid. J. P.

Groups Responsible for the Nucleal Coloration and Nucleal Reaction. R. FEULGEN and K. VOIT (*Z. physiol. Chem.*, 1924, **137**, 272—286).—Thymus-nucleic acid on mild partial hydrolysis gives rise to purines and substances which give an intense violet coloration with fuchsin–sulphurous acid and also the green pine-shaving reaction. The carbohydrate residue of thymus-nucleic acid

is not a hexose, but a substance of unknown constitution. The nucleal reaction is not caused by furfuraldehyde, but is absolutely specific for (partly hydrolysed) thymus-nucleic acid. The substance which gives these reactions is very sensitive to acids, and on further hydrolysis ceases to give the colorations. It appears to be of the nature of thyminic acid (A., 1918, i, 413), which gives intense colorations with these tests (cf. this vol., i, 438). The isolation and determination of the nature of the carbohydrate residue in thymus-nucleic acid is rendered difficult as it readily decomposes, unlike the pentoses, under the influence of acids. The carbohydrate, like the furfuraldehyde derivatives (A., 1896, i, 144), gives the green pine-shaving reaction. This reaction is due to the presence of a free aldehyde grouping in thyminic acid, and is not given when the latter is oxidised or combined with another group, and therefore thymus-nucleic acid itself does not give this coloration. D. R. N.

Nature and Significance of the Lipoids of Protoplasm. W. BIEDERMANN (*Pflüger's Archiv*, 1924, **202**, 223—258; from *Chem. Zentr.*, 1924, i, 2151).—Plant and animal protoplasms contain considerable quantities of lipoids, principally phosphatides of the lecithin type. They are probably held in adsorptive combination. Artificial digestion may be used to liberate them for analytical purposes. Lipoids exerting a protective effect against digestion occur not only in limiting membranes, but also within the protoplasm of plants. Animal protoplasm loses its resistance to digestion after death or injury. Plant protoplasm, however, retains this property so long as the lipoids are not extracted. G. W. R.

Molecular Stability of Acetic-choleic Acid. C. T. MÖRNER (*Z. physiol. Chem.*, 1924, **138**, 177—183).—Two samples of acetic-choleic acid were kept for a prolonged period in desiccators, one over sulphuric acid, and the other over sulphuric acid and quicklime. In both there were observed (1) a continuous decrease in weight, (2) at first a fall and then a rise in the melting point. The molecular weight increased in the course of the experiment (306 days) from 226 to 353. These changes indicate a continuous decomposition with loss of acetic acid, and the result is in contradiction to the claim of Wieland and Sorge (A., 1916, i, 710) regarding the extreme stability of acetic-choleic acid. C. R. H.

Fugutoxin. F. ISHIWARA (*Arch. exp. Path. Pharm.*, 1924, **103**, 209—222).—Pure fugutoxin from the ovary of *Spheroides* melts at 120°, has $[\alpha]_D^{\text{in}}$ +17° to +27°, and exhibits chemical properties which suggest that it is a glucose ester and not a glucoside. It yields an osazone of m. p. 207·5°. J. P.

Spermine. III. F. WREDE (*Z. physiol. Chem.*, 1924, **138**, 119—135; cf. this vol., i, 77, 78).—From human semen the author has isolated the *chloroaurate* of a base which proves to be identical with the spermine described by Schreiner (A., 1879, 72). This salt crystallises in leaflets which darken at 210° and melt at 216—218° (decomp.). The *chloroplatinate* forms orange plates which darken at 235° and melt at 242°. The *picrate* sublimes at 200° and melts

at 240° (decomp.); the *picrolonate* sublimes at 240° and decomposes at 280°. The *m*-nitrobenzoyl derivative has m. p. 171°. Molecular-weight determinations on the *m*-nitrobenzoyl derivative give values about 800, whence the formula of the base becomes $C_{10}H_{26}N_4$. C. R. H.

Lignoceric Acid. P. A. LEVENE, F. A. TAYLOR, and H. L. HALLER (*J. Biol. Chem.*, 1924, **61**, 157—161).—The earlier conclusions (A., 1913, i, 1151; 1914, i, 1123) that lignoceric acid differs in constitution from *n*-tetracosanic acid, subsequently criticised by Brigl and Fuchs (A., 1922, i, 712), are now confirmed by the preparation from distinct sources of two samples of the acid, which, separately and when mixed, melted at 80·5—81°, both before and after the fractional crystallisation described by Brigl and Fuchs. C. R. H.

Egg of *Bombyx Mori*—Proteins, Reactions. L. PIGORINI (*Arch. Farm. sper. Sci. aff.*, 1924, **37**, 221—230).—The eggs of the silkworm appear to contain (1) albumins, (2) globulins, (3) vitellins and nucleo-proteins, and (4) a substance allied to the ovomucoid of birds' eggs. During incubation of the eggs, the compounds of group (1) remain practically constant in amount until two days before hatching and then diminish considerably, those of groups (2) and (4) decrease slightly throughout the whole period of incubation and to a greater extent during the last two days, and those of group (3) increase continuously during the incubation; apparently the last compounds are those which are utilised principally in the formation of cytoplasm in the embryo. Except during the last two days of the incubating period, the ratio of the amount of albumins to that of globulins in the egg has the approximate value 1 : 0·7. The acidity of the alcoholic extract of the eggs, calculated as grams of oxalic acid per 100 g. of the eggs, increases from 4·536 before incubation to 5·166 at the seventh to ninth day and then falls to 2·709 at the end of the incubation on the twentieth day. T. H. P.

Imitation of Nervous and Cellular Tissue by means of Potassium Hydroxide, Silica, and Alcohol. L. A. HERRERA (*Atti R. Accad. Lincei*, 1924, [v], **33**, i, 510—512).—A solution of 1 g. of potassium hydroxide and 1 g. of lactose in 50 g. of absolute alcohol dissolves the silica gel prepared by adding alcohol to potassium silicate. When such solutions are suitably dried, almost exact imitations of nervous and cellular tissues are obtained. T. H. P.

Precipitation of the Casein of Human Milk. F. DEMUTH (*Biochem. Z.*, 1924, **150**, 144—148).—In the presence of suitable buffer mixtures the precipitation of the casein of human milk can be brought about constantly and rapidly, the optimum p_H being about 4·5. C. R. H.

Presence of a Hitherto Undescribed form of Urea in Human Urine. W. O. MOOR (*Biochem. Z.*, 1924, **149**, 575—584).—In preparing urea from human urine a non-crystalline residue is

obtained which consists of two substances, namely a crystalline urea and another non-crystalline substance isomeric with urea. This residue is soluble in water, in absolute alcohol, and in methyl and amyl alcohols, but is insoluble in ether and in chloroform. It contains a basic and an acidic substance. The former combines with oxalic acid, the latter with barium oxide. The barium salt of the acid substance contains nitrogen and sulphur. On shaking the residue with charcoal, the acid substance is adsorbed, whilst the other substance is converted into ordinary crystalline urea. The blue reaction given by urine with ammonia and phosphotungstic acid is due to the presence of the above residue. S. S. Z.

Ionic Acidity in Normal Human Urine. Influence of Food. P. Le Noir and A. M. de Fossey (*Compt. rend.*, 1924, **178**, 2008—2010).—The hydrogen-ion concentration of the urine of a normal person varies as a result of ingestion of food. During a meal, gastric secretion is accompanied by a decrease in urinary acidity in all cases where a normal mixed diet is taken. This phase is succeeded by increase of acidity, the extent and duration of which vary with different subjects and are not constant even in the same individual. H. J. E.

Effect of Phosphoric Acid on Excretion of Chlorine. W. Röckemann (*Arch. Kinderheilk.*, **72**, 161—171; from *Chem. Zentr.*, 1924, i, 1405).—The excretion of chlorine in urine and fæces is diminished after administration of sodium dihydrogen phosphate. G. W. R.

Uric Acid Excretion in the Dog. L. Rosenfeld (*Z. physiol. Chem.*, 1924, **138**, 276—279).—The oral administration of 15 g. and 7·5 g. of uric acid on two separate occasions led to approximately the same (small) increase in excretion of uric acid and total nitrogen, which bears no relation to the amount of uric acid ingested. C. R. H.

Influence of Guanylic and Adenylic Acids on Uric Acid Excretion. L. Rosenfeld (*Z. physiol. Chem.*, 1924, **138**, 280—287).—Intravenous administration of the sodium salts of guanylic and adenylic acids to dogs and rabbits led to a smaller increase in uric acid excretion and a larger increase in total nitrogen excretion than could be accounted for theoretically by the amount of substance injected. C. R. H.

Effect of Salts of the Rare Earths on the Excretion of Uric Acid. Pompeani (*Compt. rend. Soc. Biol.*, 1924, **90**, 2—4; from *Chem. Zentr.*, 1924, i, 1557).—Salts of thorium, cæsium, and didymium, subcutaneously administered, were without effect on the excretion of uric acid. Some effect was observed with salts of samarium and yttrium. G. W. R.

Creatinine Content of the Urine of Healthy and Sick Children. A. Lorenzini (*Bull. Sci. Med.*, 1922, **10**, 245—264; from *Chem. Zentr.*, 1924, i, 1555).—The creatinine content of the

urine is generally smaller in children than in adults. Data are given for the influence of certain diseases on the amounts of creatine and creatinine found in the urine. G. W. R.

Creatinine Excretion of Various Domestic Mammals. J. Szende (*Biochem. Z.*, 1924, **149**, 566—571).—The following are the average figures for the creatinine content of 1000 c. of urine: dog 1·87 g., cat 1·76 g., cattle (stall) 3·98 g., cattle (after killing in slaughter-house) 9·41 g., horse 3·59 g. Paralytic hæmoglobinæmia and tetanus raise considerably the creatine content of horse's urine. S. S. Z.

Urinary Pigment in Normal and Pathological Conditions. H. Fischer and W. Zerweck (*Z. physiol. Chem.*, 1924, **137**, 176—241).—Urochrome can be prepared in quantity by concentrating in vacuum to a syrup large volumes of normal urine. The crystalline mass is filtered off and the syrupy mother-liquor containing most of the pigment submitted to dialysis. The pigment, which is not dialysable, is then isolated from the dialysed solution by acidification, when it is obtained in amorphous flocks. Analysis gave C=52%, H=6%, N=11%, and S=2% (cf. A., 1907, i, 993; 1909, i, 920; 1923, i, 417). It is sparingly soluble in water and most organic solvents. On hydrolysis with hydrochloric acid, it yields tyrosine, leucine, histidine, and arginine. Contrary to previous observations, pyrrole does not appear to be present in the pigment and also Ehrlich's aldehyde reaction in both acid and basic fractions of the hydrolytic products was negative. Trypsin had no effect on the pigment. The amino-nitrogen content of the pigment according to Van Slyke's method amounted to 10% of the total nitrogen. The conclusion is drawn from these results that the colouring matter is definitely a protein derivative. A brown pigment from a case of porphyrinuria was also isolated. It differs from the pigment in normal urine in that it is readily adsorbed on aluminium hydroxide, from which it can be removed by means of ammonia, and precipitated from the ammoniacal solution by acidification as in the case of the normal pigment. Its elementary composition and the examination of its products of hydrolysis suggest that the two are very closely related. The content of the brown pigment is always dependent on the porphyrin content of the urine and the two vary together. It is believed that both pigments are derived from a chromoprotein present in muscle, the porphyrin originating from its prosthetic constituent and the brown pigment from the protein moiety. D. R. N.

Conversion of Urobilinogen into Urobilin. S. Biro (*Biochem. Z.*, 1924, **149**, 459—467).—Urobilin cannot be detected in freshly collected urine containing urobilinogen. The latter becomes gradually converted into urobilin both in the presence and in the absence of light. This conversion takes place also when Ehrlich's reagent is added to the urine, and can be followed spectroscopically. S. S. Z.

Volatile Fatty Acids in Fæces. A. CECCHINI (*Arch. patol. clin. med.*, 1923, **2**, 361—392; from *Chem. Zentr.*, 1924, i, 2166—2167).—Volatile fatty acids in fæces are not necessarily derived from fats and carbohydrates, but can arise from the bacterial decomposition of amino-acids. They are generally present in inverse relationship to indican in the urine. Acetic and butyric acids are commonly present but formic acid is never found. Saline aperients do not alter the bacterial flora of the intestine. From the occurrence, in certain cases, of butyric acid in urine, it is concluded that resorption of the toxic products of intestinal fermentation can take place. G. W. R.

Elimination of Methyl Alcohol and the Conditions for its Accumulation. E. M. P. WIDMARK and N. V. BILDSTEN (*Biochem. Z.*, 1924, **148**, 325—335).—The rabbit excretes methyl alcohol in constant amount in unit time independently of the concentration in the blood in such a way that the amount present in the latter, y, at a time, t, after the injection is expressed by the equation $y=(b-\beta)t$, where b is the amount administered and β the amount eliminated. The conditions for the accumulation of the alcohol in man are discussed. J. P.

Content of Calcium and Magnesium in Cancerous Blood. L. BLUM and A. KLOTZ (*Compt. rend. Soc. Biol.*, 1923, **89**, 1335—1336; from *Chem. Zentr.*, 1914, i, 1553).—In the majority of cases cancer had no effect on the calcium and magnesium content of blood. G. W. R.

Composition of Blood in Epilepsy. G. PEZZALI (*Rif. med.*, 1923, **39**, 433—437; from *Chem. Zentr.*, 1924, i, 929).—In epileptic blood there is no marked change in residual nitrogen, sugar, and chlorine. A definite decrease in cholesterol and fat, succeeded by a slight increase, and a marked increase in calcium and, frequently, of indican occur during the attack. G. W. R.

Deficiency of Calcium Ions in the Blood of Epileptics. E. J. BIGWOOD (*Compt. rend. Soc. Biol.*, 1924, **90**, 98—100; from *Chem. Zentr.*, 1924, i, 1947; cf. this vol., i, 680).—The relationship between p_H and p_{Ca} is not affected by epilepsy. After administration of sodium borotartrate alkalosis persisted whilst p_{Ca} remained within physiological limits. In such cases, convulsions do not occur. They are associated more with calcium shortage than with alkalosis. Similar conditions obtain in tetany. G. W. R.

The Amount of Calcium in the Blood and of Amino-acids in the Serum in Cases of Struma and Myositis Ossificans. A. SZENES (*Mitt. Grenzgeb. Med. Chirurg.*, 1923, **36**, 591—605; from *Chem. Zentr.*, 1924, i, 2164—2165).—The effect of different types of struma on the calcium content of the total blood and the refractive index of the serum is described. In general, the former is above normal and the latter lower with large than with small tumours and highest with malign tumours. The amino-acid content of the serum was above normal in two cases of large tumours,

In a case of myositis ossificans a high calcium content in the blood was observed. G. W. R.

Significance of Ions in Muscle Function. III. Influence of Various Cations on the Chemical Activity of Striated Frog Muscle. H. LANGE (*Z. physiol. Chem.*, 1924, **137**, 105—153).—Muscular contraction is accompanied by a series of changes of chemical and colloidal nature. Lactacidogen is converted by enzymic decomposition into free phosphoric and lactic acids which further bring about physical transformations in the muscle fibre and the covering membrane. This dissimilatory phase is followed by a rapid re-synthesis of the active substance. The chemical transformations in the muscle fibre for the time being control the absorptive condition of the sarcoplasm, and similar processes in the latter regulate the lactacidogen metabolism in the fibre. The cations may be divided into two groups according to their influence on the lactacidogen metabolism in fresh muscle. The first group, which displaces the enzyme equilibrium towards the synthetic side, comprises calcium, barium, and strontium and the second group, which does not possess this property or exhibits a contrary effect, comprises sodium, potassium, ammonium, and magnesium. The action of calcium at different concentrations varies remarkably, promoting synthesis strongly at some, and at others even showing a feeble contrary effect. On the other hand, magnesium, potassium, and sodium, especially at higher concentrations, inhibit the decom position of lactacidogen, whilst potassium even promotes its synthesis. Calcium ions behave differently from other ions ($Na^{\cdot}$, $K^{\cdot}$, and $Mg^{\cdot\cdot}$) in inhibiting the formation of lactic acid. Calcium ions strongly accelerate the decomposition of glycogen, and sodium, potassium, and magnesium ions act similarly, although to a much smaller extent. Calcium ions inhibit strongly oxidative processes, whilst potassium chloride behaves differently in producing at first a very rapid transitory increase in respiratory activity. The action of all these ions is controlled very largely by the hydrogen-ion concentration. The action of salts is due to their influence on the colloidal conditions of the tissue as well as to their effect on the enzymes. D. R. N.

Significance of Ions in Muscle Function. IV. Enzymic Synthesis of Lactacidogen under the Influence of Ions. G. EMBDEN and C. HAYMANN (*Z. physiol. Chem.*, 1924, **137**, 154—175).—The course of lactacidogen metabolism in the press juice of frog's muscle is influenced strongly by the addition of inorganic salts, both by the anions as well as the cations; CNS', I', and Cl' accelerate the degradation of lactacidogen, whilst fluorine, citrate, and calcium ions induce strongly the synthesis of lactacidogen. Thus lactacidogen synthesis under the influence of fluorine ions can be easily followed by the almost complete disappearance of inorganic phosphoric acid and by the isolation of its characteristic osazone. By the simultaneous addition of glycogen the lactacidogen synthesis is so strongly favoured that inorganic phosphoric acid, even when present in minute amounts, disappears; dextrose and

maltose have no such influence. The maximum amount of synthesis of lactacidogen under the influence of fluorine ions is obtained within the first few hours and thereafter the inorganic phosphoric acid content again gradually increases. D. R. N.

Diffusion of Glucose in the Organism. A. CHAUFFARD, P. BRODIN, P. ZIZINE, and A. GRIGAUT (*Compt. rend. Soc. Biol.*, 1923, **88**, 1022—1024; from *Chem. Zentr.*, 1924, i, 1408).—The diffusibility of glucose through animal membranes is considerably less than that of sodium chloride, sodium urate, and carbamide, respectively. The content of different physiological fluids in diffusible substances is compared. G. W. R.

Electrolytes of High Molecular Weight and their Significance in the Cell. H. HAMMARSTEN (*Biochem. Z.*, 1924, **147**, 481—543).—Pure disodium guanylate was prepared by hydrolysis of sodium (yeast) nucleinate ("Astra") in an autoclave with 5% sodium hydroxide for 30 minutes at 100° in the presence of sodium acetate. Disodium guanylate was completely precipitated at 0° by the addition of acetic acid, and was further purified by Feulgen's method. From the disodium salt guanylic acid was obtained by precipitation as the copper salt and treatment of the latter with hydrogen sulphide. The partly precipitated acid was separated from copper sulphide by means of barium hydroxide solution and was finally liberated from the barium salt by sulphuric acid. Guanylic acid has a dissociation constant of $4{\cdot}45\times10^{-3}$. Disodium guanylate dissociates as does a normal inorganic bivalent salt, and the migration velocity of the bivalent guanylate ion at 20° is 48·3. The free acid and its sodium salt have osmotic pressures which agree with the Arrhenius–van't Hoff theory, and that of the salt is lowered by sodium and magnesium chlorides, more especially by the latter. Guanylic acid only shows typical amphoteric behaviour in strongly acid solutions or when present in large excess. Strongly basic amino-acids or proteins (lysine, histone chloride) form salt-like combinations with guanylic acid which are readily split up by dialysis in the presence of neutral salts. Glycocholic acid has $k=4{\cdot}0\times10^{-5}$, whilst taurocholic acid is a much stronger acid. Extending these investigations to histone and protamine chlorides, and to the sodium and alkylammonium salts of glycocholic, taurocholic, and thymus-nucleic acids and of Congo-red and related dyestuffs, it is concluded that in such electrolytes of high molecular weight, osmotic pressure is dependent not only on the degree of dissociation, but also on the molecular volume of the substance, and is often less than the Arrhenius–van't Hoff and Bjerrum–Debye theories demand. The amount of this abnormality in osmotic pressure is a function of the ratio of the ionic volume of the larger ion to that of the smaller—if the latter is increased the osmotic pressure rises. Importance is attached to such osmotic studies in relation to the biochemistry of the living cell. J. P.

Effect of Phosphates in (Magnesium) Narcosis. K. SPIRO (*Klin. Woch.*, 1923, **2**, 2039; from *Chem. Zentr.*, 1924, i, 1410).—Injection of phosphates neutralises magnesium narcosis. G. W. R.

Effect of Veratrine on the Intestines and the Uterus and Importance of Potassium and Calcium Ions in this Connexion. E. L. BACKMAN (*Compt. rend. Soc. Biol.*, 1924, **90**, 128—131; from *Chem. Zentr.*, 1924, i, 1560—1561).—Veratrine raises the tone of the musculature of the surviving intestine and uterus of rabbits and guinea pigs. Calcium in small doses strengthens this action whilst in large doses it acts in the opposite sense. Potassium also antagonises the effect of veratrine. G. W. R.

Action of *p*-Dihydroxycamphane (Bredt). H. LEO (*Arch. exp. Path. Pharm.*, 1924, **103**, 135—137).—The increased action on the heart and on respiration of *p*-hydroxycamphor as compared with camphor and diketocamphane is not shown on introducing a second hydroxyl group, as in *p*-dihydroxycamphane, but is, on the contrary, abolished, and this new compound exhibits, indeed, a strong paralysing effect. J. P.

Diuretic and Antidiuretic Effects of Pituitary Extract. W. G. MACKERSIE (*J. Pharm. Exp. Ther.*, 1924, **24**, 83—99).—It is suggested that the effect of pituitary extract on the rate of urinary secretion may be of use as a supplement to the uterine test for this substance, since such substances as histamine and ergotoxin, the presence of which may lead to confusion in the uterine test, have no effect on the secretion of urine. C. R. H.

Increased Absorption of Cholesterol in the Presence of Deoxycholic Acid. R. SCHÖNHEIMER (*Biochem. Z.*, 1924, **147**, 258—263).—The administration to rabbits and guinea-pigs of sodium deoxycholate along with fat produces a marked increase in the rate of absorption of the latter and a pronounced lipæmia. Rabbits on a cholesterol–fat diet to which the bile salt is added show a marked increase in serum cholesterol, which is not evident if no sodium deoxycholate, or if it alone, is given. J. P.

Chemistry and Pharmacology of Kawa-kawa (*Piper methysticum*. K. SCHÜBEL (*Arch. exp. Path. Pharm.*, 1924, **102**, 250—282).—Kawa resin has a weak narcotic action, paralyses sensory nerves, and first stimulates and then paralyses smooth muscle. The hydrolysis products of the resin show similar actions. The local anæsthetic action is ascribed to compounds of the benzoic and cinnamic acid group. Kawa root contains no glucosides, nor were alkaloids detected in the resin, although nitrogen is present. From the hydrolysis products of the resin was isolated kawaic acid, $CHPh{:}CH{\cdot}CH{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CO_2H$, yellow needles or plates from benzene, m. p. 165° (decomp.) (cf. Borsche and Roth, A., 1921, ii, 862). The ethyl ester, tasting of pepper, was prepared. Kawaic acid produces an increased reflex excitability and a diminished blood pressure. By vacuum distillation of the residue from the crystallisation of kawaic acid were obtained (1) a pale yellow oil containing nitrogen and tasting of pepper, which possessed a weak narcotic action, and stimulated the digestive glands, and (2) a crystalline, unsaturated acid, m. p. 51—53°, with no narcotic action. J. P.

Mechanism of Catalytic Action of Iron Salts. I. O. BAUDISCH and L. A. WELO (*J. Biol. Chem.*, 1924, **61**, 261—274).—A review of previously published work by the author and others on the catalysis of oxidations and reductions by iron salts. C. R. H.

β-Oxidation in the Kidneys. I. SNAPPER and A. GRÜNBAUM (*Biochem. Z.*, 1924, **150**, 12—17).—After perfusion of the isolated kidneys of various animals with blood to which had been added phenylacetic acid or phenylbutyric acid there was obtained in the perfusion fluid phenylaceturic acid, whereas the perfusion of phenylpropionic acid or phenylvaleric acid led to the formation of hippuric acid, thus showing that β-oxidation (Knoop, A., 1905, ii, 46) can take place in this organ. C. R. H.

Copper, Enzymes, and Fertilisation. O. GLASER (*Biol. Bull. Marine Biol. Lab.*, 1923, **44**, 79—104; from *Chem. Zentr.*, 1924, i, 2281—2282).—Eggs of *Arbacia* absorb copper ions from sea-water to which copper sulphate is added. Copper is also a normal constituent of *Arbacia* eggs and increases in amount up to maturity. After fertilisation the copper content decreases probably owing to secretion of pigment. G. W. R.

Hydrolysis of Nucleic Acid by Takadiastase. J. NOGUCHI (*Biochem. Z.*, 1924, **147**, 255—257).—Takadiastase contains nucleinase and nucleotidase, capable of hydrolysing yeast and thymus-nucleic acids with the liberation of phosphoric acid and purine bases. J. P.

Effect of α- and β-Methylglucosides on Taka-invertase. Y. HATTORI (*Biochem. Z.*, 1924, **150**, 150—158).—The hydrolysis of sucrose by the invertase of takadiastase is inhibited by β-methylglucoside and unaffected by α-methylglucoside, whereas the reverse is true of yeast invertase. The type of inhibition, as shown by the time relations of the reaction, resembles that brought about by lævulose. C. R. H.

Participation of Co-zymase in the Degradation of Sugar. K. MYRBÄCK and H. VON EULER (*Ber.*, 1924, **57**, [*B*], 1073—1076).—The co-enzyme content of a bottom yeast was diminished by about 55% by desiccation under the conditions usual in practice, but remained almost unchanged when the specimen was rapidly spread in a thin layer on porous clay. The presence of co-zymase was established in a *Torula* from kefir, which produces alcohol, in a product from the same source which ferments lactose, yielding unknown substances, and in *Streptococcus lactis*. Its presence could not be established in *Penicillium glaucum* or *Bacillus lactis aerogenes*. H. W.

Fermentation Co-enzyme (Co-zymase) of Yeast. IV. K. MYRBÄCK and H. VON EULER (*Z. physiol. Chem.*, 1924, **138**, 1—10).—Further experiments on the purification of the co-enzyme, using mainly the lead acetate method (this vol., i, 918), are recorded. Baryta, in contrast to lead acetate, precipitates

only insignificant amounts of the co-enzyme. Adsorption by alumina gave inconclusive results. Tholin's results (A., 1922, i, 305) on the inactivation of the co-enzyme by heat at varying degrees of acidity have been confirmed with more active preparations. E. S.

Formation of *l*-Malic Acid in Alcoholic Fermentation by Yeast. H. D. DAKIN (*J. Biol. Chem.*, 1924, **61**, 139—145).—*l*-Malic acid is a constant product of the action of yeast on pure sucrose solutions; the amount formed is increased by the addition of sodium hydrogen carbonate to the medium; it is diminished by the addition of monoamino-acids, and of glutamic, aspartic, and hydroxyaspartic acids, also by the products of hydrolysis of yeast; it is little affected by proline and hydroxyproline and is sometimes increased by hydroxyglutamic acid; it is markedly increased by sodium fumarate, but is not affected by sodium succinate. C. R. H.

"Limit" Dextrin and a Complement of the Amylases. III. H. PRINGSHEIM and A. BEISER (*Biochem. Z.*, 1924, **148**, 336—343).—In continuation of previous observations (this vol., i, 106), it is found that amylose is hydrolysed by amylases much more quickly than is amylopectin. The presence of complement does not influence the hydrolysis of amylose, whilst it has a marked accelerating effect on that of amylopectin. "Limit" dextrin ("Grenzdextrin") is a trisaccharide derived from amylopectin (cf. Pringsheim and Wolfsohn, this vol., i, 714). Amylase complement has a marked effect on the hydrolysis of glycogen, a fact supporting the view that amylopectin and glycogen may be related (Pringsheim and Goldstein, A., 1922, i, 633). Complement is associated with malt amylase in the natural state. J. P.

Dextrin-producing Power of Malt Amylase and the Reactivation of Amylase Inactivated by Heat. T. CHRZĄSZCZ (*Biochem. Z.*, 1924, **150**, 60—92).—The preparations of amylase were obtained from barley, wheat, and millet, and showed only quantitative differences in their behaviour. The hydrolysis of starch by this amylase proceeds best at p_H 4·66—5·28. The speed of the reaction is increased by using large amounts of enzyme in concentrated solution and by keeping the starch paste as thick as is consistent with thorough mixing with the enzyme. The starch paste is best prepared by heating at a temperature above 80°. The optimum temperature for the reaction is not fixed, but depends on the amount of enzyme present; with small amounts it is 30—50°; with large amounts 50—70°. Amylase is completely inactivated by heating for 2 hours at 90°; such a preparation may be partly reactivated by shaking with air; shaking with oxygen, hydrogen peroxide, or carbon dioxide does not increase the reactivation. C. R. H.

Isoelectric Point of Malt Amylase. H. C. SHERMAN, A. W. THOMAS, and M. L. CALDWELL (*J. Amer. Chem. Soc.*, 1924, **46**, 1711—1717).—Working with purified enzyme preparations in solutions adjusted to a wide range of hydrogen-ion concentrations

by means of buffer solutions, and using the U-tube apparatus of Michaelis (A., 1909, i, 277) suitably modified, the isoelectric point of malt amylase has been determined by electrophoresis to be p_H 4·3—4·5, a point which coincides with its maximum activity towards starch (Sherman, Thomas, and Baldwin, A., 1919, i, 181). On the acid side of this range, the enzyme migrates towards the cathode, on the alkaline side towards the anode. The relative concentration of the enzyme in the anodic and cathodic arms was determined by a modification of Sherman's gravimetric method (A., 1910, ii, 1012; 1922, i, 283). These results show that the enzyme is either an ampholyte or associated with an ampholyte and support the view previously advanced that amylase is either protein in nature or intimately associated with protein. The results are in accord with the observation (Sherman and Thomas, A., 1915, i, 183) that the amylolytic activity of malt amylase is increased by the addition of neutral salts. R. B.

Invertase in Honey. J. M. Nelson and D. J. Cohn (*J. Biol. Chem.*, 1924, **61**, 193—224).—Honeycombs were extracted with water and the filtered solution was treated with alcohol; the viscous precipitate was stirred with a little water and the filtered solution submitted to dialysis; the clear solutions of invertase so obtained were used for a detailed comparison of the mode of action of this invertase with that from yeast. The relative velocities of inversion at different periods of the reaction are not the same with the two enzymes; the optimum p_H for honey invertase is 5·5—6·3 as against 4·4—5·0 for yeast invertase; moreover, for honey invertase the optimum p_H varies with different stages of the reaction, whereas with yeast it is constant throughout. The honey invertase is the less stable towards acid, being partly inactivated at p_H 5·8. The effect of variations in sucrose concentration is similar with both enzymes, the optimum concentration being 4%. C. R. H.

Decomposition of Invertase by Enzymes. I and II. H. von Euler and K. Josephson (*Z. physiol. Chem.*, 1924, **138**, 11—20, 38—48).—Although the physical properties of invertase recall those of proteins (this vol., i, 466, 693, 799; cf., however, Willstätter and Schneider, this vol., i, 692), neither the separate nor successive actions of pepsin and trypsin produced a decrease in the viscosity of a solution of an invertase preparation of high activity ($1/f$=225) approaching in magnitude that produced in a gelatin solution. Pepsin diminished the activity of the invertase only slightly (14%) in 38 hours; trypsin, however, caused a considerable diminution in 2 days, and after 5 days only 28% of the original activity remained. The authors conclude that invertase is only decomposed with difficulty by proteolytic enzymes, but that when such decomposition does occur the activity of the invertase is simultaneously destroyed; the activity of the invertase complex is thus closely connected with its protein portion. E. S.

Invertase of *Aspergillus flavus*. K. Josephson (*Z. physiol. Chem.*, 1924, **138**, 144—147).—The hydrolysis of sucrose by this

mould follows the course of a unimolecular reaction; the curve expressing relationship of rate of hydrolysis to p_H lies between those obtained with the invertases of yeast and of *Penicillium glaucum*. C. R. H.

Lichenin and Lichenase. H. PRINGSHEIM and W. KUSENACK (*Z. physiol. Chem.*, 1924, **137**, 265—271).—The swelling of lichenin is due to the fact that it forms an ester with silicic acid. A lichenin preparation purified by repeated solution and precipitation contained 2·64% of ash which consisted of silica only. The presence of silica as an adventitious impurity in lichenin thus purified is scarcely conceivable. In order to ascertain whether lichenin is entirely composed of cellobiose residues, it was hydrolysed with the lichenase recently found in malt extract (this vol., i, 233), which also contains cellobiase. Further observations now show that cellobiase disappears completely after keeping the malt extract for 6 months, and it then contains lichenase only. When lichenin is hydrolysed with such an extract at 37° and p_H 5, it is quantitatively converted into cellobiose in about 4 days. Cellobiose on acetylation in pyridine solution does not give β-octa-acetylcellobiose, m. p. 228°, but the α-form, m. p. 195°. D. R. N.

Laccase. P. FLEURY (*Bull. Soc. Chim. biol.*, 1924, **6**, 436—448; 449—463).—The oxidation of guaiacol by laccase was studied quantitatively by determining colorimetrically the guaiacoquinone formed. The latter is proportional to the time or the quantity of the enzyme so long as the action is carried out at a moderate temperature and not too far. When the "initial velocity" (or activity) of the enzyme is plotted against the concentration of guaiacol, keeping the quantity of enzyme constant, a curve is obtained which may be divided into two parts, the first in which the velocity is proportional to the quantity of guaiacol, and the second in which it is independent of its concentration. When the amount of laccase is varied, the point of inflexion of the curve is displaced towards lower concentrations with diminishing amounts of laccase. The influence of the oxygen concentration is very similar to that of guaiacol. The results may be explained by assuming a combination between the enzyme and the substrate, or by the influence of the rate of diffusion of oxygen into the medium. D. R. N.

Comparison of Liver Esterase with Pancreatic Lipase. Stereochemical Specificity of Lipases. R. WILLSTÄTTER and F. MEMMEN (*Z. physiol. Chem.*, 1924, **138**, 216—253).—The hydrolytic activity of liver esterase, whether purified or not, towards glycerides is reduced by the addition of such substances as calcium chloride and sodium oleate which favour the action of pancreatic lipase; in the hydrolysis of simple esters the addition of these substances is without effect. A comparison of the rate of hydrolysis of different substances by the enzymes from liver and pancreas of the same animal shows that in the case of olive oil the pancreatic enzyme is enormously more active, whilst in that of methyl butyrate the liver enzyme is the more active. The best purification of the

hepatic enzyme was effected by extracting the liver with dilute ammonia, redissolving the crude product, obtained by evaporating this extract, in a solution of acetic acid and ammonium acetate of p_H 4·2, and adsorbing the enzyme on kieselguhr or aluminium hydroxide, from which it was subsequently recovered with dilute ammonia; such preparations are about twenty times as active as the crude desiccated liver; on keeping they lose about one-fifth of their activity in the first few days and thereafter remain almost constant. The activity of the enzyme, especially of the purified preparations, is strongly inhibited by atoxyl, and slightly by quinine.

A series of experiments was made to determine the stereochemical specificity of the two enzymes (cf. Dakin, A., 1904, i, 1071; 1905, i, 556). Pancreatic lipase hydrolysed the lævorotatory component more rapidly in the case of the racemic esters of mandelic, phenylmethoxyacetic, phenylchloroacetic, and phenylbromoacetic acids and the dextrorotatory component of the esters of phenylaminoacetic and tropaic acids and of leucine; with hepatic esterase, on the other hand, the dextrorotatory component was the more rapidly hydrolysed in all the above cases except for the esters of phenylchloroacetic, phenylbromoacetic, and tropaic acids. The degree of specificity of the pancreatic enzyme was the greater throughout. The authors conclude, on the whole, that the two enzymes are distinct from one another. C. R. H.

Enzymic Activity of Lactic Acid Bacteria. II. A. I. Virtanen (*Z. physiol. Chem.*, 1924, **138**, 136—143; cf. this vol., i, 915).—Dried preparations of *Bacillus casei* ϵ possess the power of synthesising hexosephosphate from solutions containing dextrose and inorganic phosphate, which suggests a similarity between the process of lactic acid fermentation and the formation of lactic acid in muscle. C. R. H.

Activity of Urease in High Concentrations of Alcohol. N. N. Ivanov (*Biochem. Z.*, 1924, **150**, 108—114).—Urea is decomposed, to some extent, by urease in concentrations of alcohol as high as 92·5% and of acetone up to 85%. It is suggested that such solutions, in which the decomposition proceeds much more slowly than in water, may afford suitable media for the study of the intermediate products of the reaction. C. R. H.

Enzymic Hydrolysis of Phenaceturic Acid. C. Neuberg and J. Noguchi (*Biochem. Z.*, 1924, **147**, 370—371).—Takadiastase contains an enzyme capable of hydrolysing sodium phenaceturate with the liberation of phenylacetic acid. J. P.

Phenolases in the Blood. K. Hizume (*Biochem. Z.*, 1924, **147**, 216—220).—There is present in human serum a phenolase capable of oxidising dihydroxybenzene derivatives, which is affected neither by heating at 56° for 30 minutes nor by dialysis. The phenolase is also found in the sera of sheep, rabbits, dogs, and guinea-pigs in amounts diminishing in the order cited. J. P.

Enzymes of the Skin. Y. Yamasaki (*Biochem. Z.*, 1924, **147**, 203—215).—Diastase and lipase are present in human skin

in the superficial and deeper layers. The latter enzyme is stable to both quinine and atoxyl and therefore differs from the other lipases of the body. Peptolytic and autolytic enzymes are also present, together with a catalase and an oxidase, the latter being capable of oxidising dihydroxybenzene derivatives but not the monohydroxy compounds. J. P.

Formation of *l*-Leucic Acid in Acetone–Butyl Alcohol Fermentation. E. G. SCHMIDT, W. H. PETERSON, and E. B. FRED (*J. Biol. Chem.*, 1924, **61**, 163—175).—From the solution obtained by the fermentation of maize mash by *Bacillus granulobacter pectinovorum* there were isolated the calcium and zinc salts of an acid, $C_6H_{13}O_3$. On distillation with permanganate this acid gave an aldehyde, which was identified by its *p*-nitrophenylhydrazone and its aldomedon as isovaleraldehyde. The acid was was therefore α-hydroxy*iso*hexoic acid; it gives all the qualitative reactions for lactic acid, and it is suggested that it may have been this acid, and not lactic acid, which was obtained by Speakman (this vol., i, 371) under similar conditions. C. R. H.

Activation of Papain by Hydrocyanic Acid. R. WILLSTÄTTER and W. GRASSMANN (*Z. physiol. Chem.*, 1924, **138**, 184—215).—The activating effect of hydrocyanic acid on papain first observed by Mendel and Blood (A., 1910, i, 796) has been studied in a series of experiments on the hydrolysis of gelatin by this enzyme. The rate of hydrolysis is approximately trebled by the addition of cyanide; the optimum temperature for the enzyme is 65—70°, the rate of reaction being nearly doubled by every rise of 10° from 30° to 70°; the optimum reaction, with or without the addition of cyanide, is p_H 5, and it is suggested that the closeness of this optimum reaction to the isoelectric point of gelatin (p_H 4·7) may indicate that this enzyme attacks the undissociated protein molecule. The maximum activation is obtained by allowing the cyanide to act on the enzyme for an hour, before mixing with the gelatin solution; this is true of both crude and purified preparations and of those which, having been once activated with cyanide, have been inactivated again by removal of the hydrocyanic acid; it therefore shows that the activation consists in the formation of a dissociable compound between enzyme and cyanide. The sensitivity of the enzyme to the presence of cyanide is so great that it can be used as a test for the presence of amounts of cyanide of the order of 0·001 mg. Commercial peptone and peptide mixtures prepared by the partial digestion of gelatin are scarcely attacked by papain unless activated by cyanide; pure dipeptides are not hydrolysed even by the activated enzyme. The best purification of the enzyme was effected by adsorption on aluminium hydroxide from an aqueous-alcoholic solution containing ammonia, and subsequent recovery from the precipitate by means of dilute acetic acid. C. R. H.

Asymmetric Enzymic Hydrolysis of Benzoylated Amino-acids. C. NEUBERG and K. LINHARDT (*Biochem. Z.*, 1924, **147**, 372—376).—Benzoyl-*dl*-glycine and benzoyl-*dl*-alanine are hydrolysed by preparations of takadiastase, the *d*-stereoisomerides

being preferentially attacked whilst the *l*-isomerides remain unchanged. Thus it is possible to obtain both antipodes of a racemic amino-acid, since the free *d*-amino-acid may be separated from the benzoyl-*l*-amino-acid and the latter may then be hydrolysed. J. P.

Biochemical Method of Resolving Racemic Amino-acids. C. HOPPERT (*Biochem. Z.*, 1924, **149**, 510—512).—Takadiastase contains an enzyme capable of hydrolysing hippuric acid and its homologues into benzoic acid and the amino-acid. This *amino-acidase* was found by the author to hydrolyse benzoyl-*d*-alanine, but not its stereoisomeride, and he adopted this method for resolving the inactive amino-acid. S. S. Z.

Enzymes of *Utricularia vulgaris*. I. A. N. ADOWA (*Biochem. Z.*, 1924, **150**, 101—107).—Extracts of this insectivorous plant possess a slight power of hydrolysing gelatin and casein. In the case of gelatin, the hydrolysis proceeds best in an alkaline medium; in such a medium the process is inhibited by the addition of calcium chloride and of animal charcoal, but in a neutral medium it is slightly accelerated by these substances. C. R. H.

Occurrence of Catalase in Micro-organisms. A. J. KLUYVER (*Z. physiol. Chem.*, 1924, **138**, 100—101).—It is provisionally concluded that catalase occurs only in those bacteria which use free oxygen in their metabolic processes. E. S.

Destruction of Rennin by Agitation: A Case of Catalysis at an Air–Liquid Interface. E. K. RIDEAL and C. G. L. WOLF (*Proc. Roy. Soc.*, 1924, **A**, **106**, 97—116).—Agitation of rennin solutions reduces their power of clotting milk. This is traced to the presence of some substance, probably a fatty acid, which reacts chemically with the rennin, mainly at the air–liquid surface where they are both adsorbed and the molecules are orientated favourably for reaction. This substance can be removed by dialysis, and by selective adsorption by fuller's earth or starch, or it can be displaced from the surface by some capillary active substance such as saponin. It can also be rendered innocuous by conversion into a salt. Its effect can be imitated by the capillary-active organic acids or by phenol, but sulphuric acid (not capillary-active) is ineffective. As a result of the reaction the surface tension is increased and the p_H lowered. Dialysed solutions of rennin are less active owing to partial coagulation but may be peptised by small quantities of acid without the p_H being significantly increased. [Cf. *B.*, 1924, 726.] L. J. H.

Mechanism of the Anti-peptic Action of Blood Serum. L. LORBER (*Biochem. Z.*, 1924, **148**, 49—52).—The anti-peptic action of blood-serum is ascribed to the sodium hydrogen carbonate present. J. P.

Efficiency of some Organic Dyes as Anti-ferments. E. H. HARVEY (*Amer. J. Pharm.*, 1924, **96**, 585—589).—The efficiency of a number of organic dyes as anti-ferments has been measured by

observing the retardation of the change in rotation produced by their addition to yeast–sucrose solution. The following dyes are arranged in the order of decreasing efficiency: safranine, *p*-nitrophenol, methylene-blue, eosin Y, methyl-violet, cyanine, acid-fuchsin, alizarin-blue S. Mercuric chloride is the most effective anti-ferment, as it kills the yeast cells almost immediately; safranine shows 57·3% efficiency as compared with mercuric chloride, whilst that of alizarin-blue S is practially nil. Ultra-violet light shows an efficiency of 91·8%. R. B.

Action of Uranyl Acetate. II. Action on Various Enzymes. Y. MIKAWA (*Biochem. Z.*, 1924, **149**, 540—549).—Uranyl acetate reduces the action of takadiastase, serum diastase, liver diastase, blood catalase, liver catalase, serum lipase, and liver lipase. S. S. Z.

Action of Poisons on Enzymic Processes. IX. Action of Poisons on Metallic Catalysts and Catalase Processes. C. G. SANTESSON (*Skand. Arch. Physiol.*, 1923, **44**, 262—305; from *Chem. Zentr.*, 1924, i, 1964—1965; cf. A., 1922, i, 1077—1078).—From a consideration of the properties of catalases and metallic catalysts the action of catalases is held to be enzymic and not due to metals present in them. Electrolytes exert a stronger inhibitory effect on colloidal metallic catalysts than on catalases. This may be related to the protective effect of emulsoids, associated with or identical with the catalases. G. W. R.

Action of Simple Narcotics on Succinodehydrogenase. H. GRÖNVALL (*Skand. Arch. Physiol.*, 1923, **44**, 200—214; from *Chem. Zentr.*, 1924, i, 1961).—Methyl alcohol, ethyl alcohol, propyl alcohol, and the butyl alcohols inhibit the activity of succinodehydrogenase (Ohlsson, A., 1922, i, 785). The inhibitory effect increases with the number of carbon atoms. G. W. R.

Action of Urethanes on Succinodehydrogenase. D. SVENSSON (*Skand. Arch. Physiol.*, 1923, **44**, 306—314; from *Chem. Zentr.*, 1924, i, 1961; cf. preceding abstract).—Methyl-, ethyl-, propyl-, *iso*butyl-, and *iso*amyl-urethanes exert an inhibitory effect, which increases with the molecular weight of the urethane, on succinodehydrogenase. Chloral hydrate is as effective as *iso*butylurethane, whilst phenol and potassium fluoride have a still greater inhibitory power. G. W. R.

Effect of Antipyretics on Succinodehydrogenase and on the Respiration of Tissues. I. I. NITZESCU and J. COSMA (*Compt. rend. Soc. Biol.*, 1923, **89**, 1401—1402, 1406—1407; from *Chem. Zentr.*, 1924. i, 2163).—Sodium salicylate, pyramidone, and antipyrin exert an inhibitory effect on the succinodehydrogenase action of ox muscle on potassium succinate. A similar effect on the respiration of tissues is observed. Urethanes display a similar but weaker effect. G. W. R.

Mechanism of the Action of Amino Promoters on Enzymes. E. W. ROCKWOOD (*J. Amer. Chem. Soc.*, 1924, **46**, 1641—1645; cf. this vol., i, 351).—The rate of decay of urease

and ptyalin in solution, alone, and in the presence of three typical α-amino-acids, glycine, aspartic and hippuric acids, has been measured. The results confirm the view that the promoter effect is only partly due to the prevention of decay of the enzyme, and prove that the promoter acts chiefly through a specific stimulating influence on the enzyme (cf. Sherman and Walker, A., 1923, i, 1033). R. B.

Autolysis. XI. Relation of the Iscelectric Point to Digestibility. A. B. HERTZMAN and H. C. BRADLEY (*J. Biol. Chem.*, 1924, **61**, 275—287).—Addition of proteins to autolysing liver increases the amino-acid production at and above a certain hydrogen-ion concentration which is specific to each protein and almost coincident with its isoelectric point. This is taken to be evidence that in order to be digested by liver proteases, proteins must be in the form of acid salts, and it explains the previous observation (A., 1916, i, 582) that addition of acid stimulates autolysis. C. R. H.

Autolysis. II. Effect of Iodine on the Autolysis of Organs. O. STEPPUHN and L. UTKIN-LJUBOVZOV (*Biochem. Z.*, 1924, **150**, 165—172; cf. A., 1923, i, 1158).—Autolysis of serum, liver, lungs, and kidneys is accelerated by small amounts of iodine and delayed by large amounts; tryptic digestion of casein is delayed by iodine in all concentrations. C. R. H.

Oligodynamic Properties of Insoluble Mercury Compounds. S. REBELLO (*Compt. rend. Soc. Biol.*, 1923, **88**, 1333—1335; from *Chem. Zentr.*, 1924, i, 924—925).—Mercury and insoluble mercury compounds (with the exception of mercuric sulphide) exert an inhibitory effect on bacterial growth by diffusion in gel cultures. G. W. R.

Properties of Diphtheria Anatoxin. G. RAMON (*Compt. rend.*, 1924, **179**, 422—425).—Diphtheria anatoxin differs from the original toxin in having lost toxicity (cf. this vol., i, 463) and possessing a greater resistance to heat. Preparations of the anatoxin retained their strength, as measured by the amount of antitoxin required to cause flocculation, without sensible variation when kept at 3° to 4° for a year. The rate of flocculation is slightly diminished, and this effect is a little more pronounced when the anatoxin is kept at laboratory temperature (20°). The length of time for which the preparations were kept was without appreciable effect on their immunising or hyperimmunising power, *in vivo*, and in no case was any return of toxicity observed, even after the lapse of a year. Anatoxin preparations warmed at 65° or 70° for 1 hour retained their full flocculating and immunising powers, the appearance of the flocculation being more or less retarded, and these properties begin to decrease only when the preparation is heated at 72—75°. R. B.

Effect of Oxidising Agents on Diphtheria Toxin. F. DE POTTER (*Compt. rend. Soc. Biol.*, 1923, **89**, 422—425; from *Chem. Zentr.*, 1924, i, 930).—Diphtheria toxin is oxidised only with difficulty even by ozone and potassium permanganate. G. W. R.

Yeast Protein as Antigen. H. LÜERS and F. OTTENSOOSER (*Biochem. Z.*, 1924, **148**, 130—146).—From dried yeast, the proteins cerevisin and zymocasein were isolated in yields of 10% and 3%, respectively. They can be differentiated by crossed precipitin reactions, from which it is concluded that their specificity as antigens has primarily a chemical basis. Anaphylaxis experiments reveal the presence of yeast proteins as well as those of barley in the precipitate formed during the pasteurisation of beer. J. P.

Products of the Catalytic Degradation of the Feathers of the Goose. Remarks on W. S. Ssadikov and N. D. Zelinsky's Work. E. ABDERHALDEN (*Biochem. Z.*, 1924, **149**, 572—574).—Polemical. S. S. Z.

Preparation of Insulin. H. PÉNAU (*J. Pharm. Chim.*, 1924, **30**, 145—153).—Impure insulin is obtained from the pancreas by extraction with alcoholic hydrogen chloride, removing fatty impurities and a portion of the salts and proteins, and precipitation with absolute alcohol. It is purified by saturating its solution with sodium chloride, centrifuging, and dialysing the solution of the solid so obtained. The insulin so obtained does not cause harmful secondary reactions. [Cf. *B.*, Oct. 31.] W. T. K. B.

Preparation of Insulin and its Physiological Action. C. SERONO, E. TROCELLO, and A. CRUTO (*Rassegna Clin. Terap. Sci. aff.*, 1923, **22**, 243—247; from *Chem. Zentr.*, 1924, i, 1409).—Directions are given for the preparation of insulin free from diastase. It is stated that methæmoglobin occurs in the blood of rabbits under the influence of insulin. G. W. R.

Preparation of Insulin. A. SORDELLI and V. DEULOFEU (*Compt. rend. Soc. Biol.*, 1923, **89**, 743—744; from *Chem. Zentr.*, 1924, i, 1234).—The precipitate in 0·1—0·2*N* picric acid is purified by washing with acetone. The picric acid may also be removed by adsorption on silk. G. W. R.

Metabolin and the Internal Secretion of the Pancreas. E. VAHLEN (*Münch. med. Woch.*, 1924, **71**, 101—102; from *Chem. Zentr.*, 1924, i, 2178).—"Irreversible" metabolin (Gehe's "irrebolin") is effective against adrenaline glycosuria in rabbits when administered per os, and still more effective per rectum. Insulin is held to inhibit the formation of sugar in the liver, whilst "irrebolin" increases the oxidation of sugar. The complete function of the inner secretion of the pancreas is due to a combination of the actions of these two hormones. G. W. R.

Yeast Growth Promoting Vitamin Tested on Animals. J. DEAS (*J. Biol. Chem.*, 1924, **61**, 5—8).—An infusion of malt combings, which has been shown to contain the "bios" described by Wildiers (*La Cellule*, 1901, **18**, 313) and which is apparently identical with the vitamin-*D* of Funk and Dubin (A., 1922, i, 203), when administered to rats in combination with a diet free from vitamin-*B*, does not promote their growth. The "bios" and vitamin-*B* are therefore not identical. C. R. H.

Comparative Physiological Importance of Iron and Zinc. G. BERTRAND and H. NAKAMURA (*Compt. rend.*, 1924, **179**, 129—133; cf. A., 1922, i, 893).—It has already been shown that when a litter of young mice was divided into two groups, one of which was fed on a diet free from vitamins and also completely free from zinc, the other on a diet free from these vitamins but containing small quantities of zinc, the life of the latter group was prolonged 25—50% beyond that of the former. The experiments have now been repeated with both groups receiving zinc but only one group receiving iron. In only one experiment in a series of six did the iron-fed mice survive the others, and the presence of iron in the diet has not therefore the marked effect of that of zinc. F. G. M.

Colloidal Properties of Phloridzin. R. SCHAEFER and F. SCHMIDT (*Biochem. Z.*, 1924, **149**, 585—591).—Phloridzin diffuses very slowly through gelatin gels. Solutions of widely differing concentrations do not produce any perceptible lowering of the freezing point and display a strikingly low conductivity. The addition of alkali or acid does not alter its degree of dissociation. A Tyndall cone is observed in phloridzin solutions of considerable dilutions and colloidal particles can be seen with the immersion ultramicroscope. By means of the ultra-filter the dimensions of these particles are found to be probably smaller than 10 $\mu\mu$.

S. S. Z.

Characters and Composition of Mustard Oil. J. C. DELAGE (*Ann. Falsif.*, 1924, **17**, 336—343).—Specimens of mustard oil examined had d 1·0186 to 1·0237 and contained from 96 to 97·7% of allylthiocarbimide. On fractional distillation from a few drops to 7% distils at 148·5° to 149·9°; the greater part distils at 150—150·5° (pure allylthiocarbimide) and the residue amounts to 1 to 2%. The composition of mustard oil varies with its age; the maximum amount of allylthiocarbimide is present a few months after its preparation, and then decreases. W. P. S.

Insecticidal Principle in *Chrysanthemum cinerariæfolium*. IV. Insecticidal Principle Produced on Dry Distillation of *Chrysanthemum cinerariæfolium*. R. YAMAMOTO and M. SUMI (*J. Chem. Soc. Japan*, 1923, **44**, 1070—1085).—By distilling powdered flowers of *Chrysanthemum cinerariæfolium* at 260—280°, an acidic distillate was obtained, in which the following compounds were found: Acetic and propionic aldehydes and acids, methyl-, trimethyl-, butyl-, and amyl-amines, pyridine and a homologue of pyridine (picrate, m. p. 84°; chloromercurate, m. p. 125°). For determining the insecticidal power of these compounds, the effects of homologous acids, esters, and bases were compared on flies and other insects. When naturally evaporated, formic acid is more potent than any other fatty acid; butylamine and *tert.*-amylamine have the strongest action amongst amines. In the case of aliphatic amines boiling below 80°, the insecticidal power is proportional to the molecular weight. When evaporated by heating or eaten by

insects, nicotine is the most toxic of the substances investigated. Generally cyclic compounds have greater power than aliphatic substances. K. K.

Chemistry of Grape Pigments. II. Anthocyans in Clinton Grapes. R. J. ANDERSON and F. P. NABENHAUER (*J. Biol. Chem.*, 1924, **61**, 97—107; cf. this vol., i, 251).—The anthocyanin of Clinton grapes has been isolated and appears to be identical with that obtained by Willstätter and Zollinger from *Vitis riparia* (A., 1917, i, 47). It was isolated as the *picrate* which was converted into an amorphous *chloride*, $C_{23}H_{35}O_{12}Cl,2H_2O$. On boiling with hydrochloric acid it gives dextrose and crystalline *anthocyanidin chloride*, $C_{17}H_{15}O_7Cl,1{\cdot}5H_2O$. On boiling with hydriodic acid this yields delphinidin iodide; the methoxyl content is intermediate between those required by a mono- and a di-methyl ether of delphinidin. Phloroglucinol was isolated from the products of alkali fusion of the anthocyanidin chloride; the latter, on boiling with acetic anhydride, gave an acetyl derivative (m. p. 205—210°); this, on oxidation with permanganate, gave an ether-soluble substance from which, by hydrolysis with hydriodic acid, gallic acid was obtained. C. R. H.

Presence of Valine in Zein. H. D. DAKIN (*J. Biol. Chem.*, 1924, **61**, 137—138).—The presence of valine in zein, recorded by Osborne and co-workers (A., 1908, i, 115; 1910, i, 598), is confirmed by the isolation of about 1% of pure crystalline valine after hydrolysis of zein by boiling with dilute sulphuric acid. The author suggests that his own previous failure to detect valine in this protein (A., 1923, i, 1243) may have been due to racemisation owing to the high temperature at which the hydrolysis was carried out. C. R. H.

Optically Active Asparagine in Seedling Lupins. A. PIUTTI (*Atti I. Congr. naz. Chim. pur. appl.*, 1923, 384—386; from *Chem. Zentr.*, 1924, i, 1941).—*d*-Asparagine was obtained together with small quantities of *s*-asparagine from lupin seedlings. G. W. R.

Henna. O. A. OESTERLE (*Schweiz. Apoth.-Ztg.*, 1923, **61**, 541—543; from *Chem. Zentr.*, 1924, i, 1388).—From a hot alcoholic extract of henna, mannitol and tribenzacetal were isolated. It is possible that mannitol is not a normal constituent of henna. G. W. R.

Ternary Materials of Green and Etiolated Leaves. H. COLIN and H. GRANDSIRE (*Compt. rend.*, 1924, **179**, 288—291).—The green leaves of the variegated chestnut always contain starch, which is absent from the etiolated leaves, and a larger proportion of both sucrose and reducing sugars than the latter. The sugars of etiolated leaves contain a larger proportion of dextrose. At midsummer a dextrorotatory, non-reducing sugar, which is oxidised

by nitric acid to mucic acid and which, after the action of invertase, is slowly hydrolysed by emulsin, appears in the green leaves and increases in quantity up to 0·5% as the season advances. No such product is found in etiolated leaves. Both green and etiolated leaves contain at least two glucosides, æsculin and fraxin, and the quantity of fatty materials is practically the same in both. The green leaves, however, contain a larger quantity of pectins which are precipitated by alcohol, baryta, and basic lead acetate and on hydrolysis yield arabinose. J. W. B.

Essence of Iris. P. Langlais and J. Goby (*Compt. rend.*, 1924, **179**, 173—175).—The acidic constituents of iris essence have been separated by fractional distillation into octoic acid, b. p. 110—111°/4 mm., *anilide*, m. p. 51°; nonoic acid, b. p. 124—125°/4 mm., *anilide*, m. p. 57°; decoic acid, b. p. 138—139°/4 mm., *anilide*, m. p. 65·5°, ethyl ester, b. p. 104°/4 mm., d^{28} 0·859; undecoic acid, b. p. 145—146°/4 mm., *anilide*, m. p. 71°; dodecoic acid, b. p. 153—154°/4 mm., *anilide*, m. p. 75·5°; tridecoic acid, *anilide*, m. p. 81·5°. This is claimed to be the first occasion on which nonoic, undecoic, and tridecoic acids have been found in natural products. F. G. M.

Phytosterols of Wheat Endosperm. R. J. Anderson and F. P. Nabenhauer (*J. Amer. Chem. Soc.*, 1924, **46**, 1717—1721; cf. this vol., i, 924).—The unsaponifiable matter from the fat extracted from wheat endosperm has been separated into an unsaturated sterol, identical with sitosterol, a saturated sterol, dihydrositosterol, $C_{27}H_{47}OH$, m. p. 144—145°, $[\alpha]_D^{20}$ +25·82° (in chloroform), and a non-crystallisable oil which has not been examined. The two sterols cannot be separated by crystallisation of their bromination products from alcohol, but are readily separated by treatment with acetic anhydride and sulphuric acid. The dihydrositosterol gives an acetyl derivative, m. p. 140°, and appears to be identical with the saturated sterol occurring in maize endosperm. The sterol is present throughout the wheat endosperm, but especially in the bran. R. B.

Effect of Germination on the Aleurone Layer. E. B. Bennion (*Cereal Chem.*, 1924, **1**, 179—183).—A section of the aleurone layer from an ungerminated wheat grain placed on purified starch and kept moist showed no diastatic action in 8 days. From this and other experiments, it is concluded that the aleurone cells of the wheat grain are not glandular in the same sense as the epithelial cells of the scutellum; they provide a reserve food supply but do not function until 6 days after germination.

Analyses of barley and wheat after definite periods of germination showed a gradual decrease in nitrogen content after 30 hrs. Subsequently, in the case of wheat, after about 220 hrs. there is a rapid increase in percentage of nitrogen due to the complete utilisation of the starch in the endosperm. During the early stages of germination, amides formed by the degradation of proteins are further broken down and ammonia is evolved. C. I. G.

Zinc and Copper Compounds of Phæophytin. R. Willstätter and K. Sjöberg (*Z. physiol. Chem.*, 1924, **138**, 171—176).—By the action of zinc acetate in glacial acetic acid solution a compound was obtained containing 1 mol. of zinc to 2 mols. of phæophytin; in pyridine solution 1 mol. of zinc combined with 1 mol. of phæophytin. Two copper compounds were prepared in similar ways, both of which contained 1 mol. of copper to 1 mol. of phæophytin. On hydrolysis with methyl-alcoholic potassium hydroxide, both zinc compounds gave zinc compounds of phytochlorin E and phytorhodin G which were easily decomposed by hydrochloric acid; the copper compound prepared in glacial acetic acid behaved similarly, but that prepared in pyridine solution gave copper derivatives of the hydrolysis products which were very stable towards hydrochloric acid. C. R. H.

Wine Yeasts. E. Kayser and H. Delaval (*Compt. rend.*, 1924, **179**, 295—297).—The authors have isolated and described several strains of red yeasts from the vine "Breton," two of which are bottom yeasts, producing red colonies, and a third a top yeast forming pigments most intensely in the presence of slightly fermentable or non-fermentable sugars. These yeasts liquefy gelatin, and ferment lævulose, dextrose, and sucrose, but neither lactose nor raffinose. They ferment lævulose more readily than dextrose, the reverse being the case with a colourless yeast of the same origin. They are equally sensitive to the presence of nitrogenous substances (cf. Kayser, A., 1912, ii, 861) and produce a relatively larger proportion of volatile esters than does the colourless yeast. The ratio of valeric acid to acetic acid in the case of the red yeasts is also twice that obtained with the colourless variety. J. W. B.

Formation of Starch from Sugar by the Leaves of Higher Plants. A. W. Reinhard (*Compt. rend. Soc. Biol.*, 1923, **89**, 1274—1275; from *Chem. Zentr.*, 1924, i, 1548).—The leaves of beans, peas, and white acacia produce starch when immersed in 10% sugar solution and exposed to light. G. W. R.

Transformation of Hydrocyanic Acid by Plant Sap. S. Dezani (*Biochim. terap. sperim.*, 1923, **10**, 85—96; from *Chem. Zentr.*, 1924, i, 2159).—Plant sap produces substances which on treatment with alkalis yield ammonia from hydrocyanic acid. This property is not shown by fermented plant juices or after addition of dextrose on account of the high acidity produced. G. W. R.

Reactions of the Alga *Chondrus crispus*, particularly with certain Dyes used in Therapy. E. Justin-Mueller (*J. Pharm. Chim.*, 1924, **30**, 154—161).—The action of various acids, bases, salts, and dyestuffs on an aqueous extract of the alga is described. Flocculation is caused by azines (*e.g.*, safranine) and thiazines (*e.g.*, methylene-blue), but not by oxazines (*e.g.* Meldola's-blue) nor by methyl violet or magenta. W. T. K. B.

Detection of Acids in Plants. II. H. SCHMALFUSS and K. KEITEL (*Z. physiol. Chem.*, 1924, **138**, 156—163).—A detailed description is given of a method of qualitative separation of the acids which may be obtained from plants, and also of micro tests for certain individual acids. C. R. H.

Method for Preparing Large Quantities of Yeast Nucleic Acid as a Magnesium Compound. E. J. BAUMANN (*J. Biol. Chem.*, 1924, **61**, 1—4).—Yeast is extracted with water, the solution made alkaline with sodium hydroxide, then partly neutralised with hydrochloric acid, and finally acidified with acetic acid; to the filtered solution is added magnesium sulphate to make 5% concentration and hydrochloric acid until precipitation is complete. The preparations so obtained are protein-free, but contain somewhat less than the theoretical nitrogen and phosphorus; the yield is 0·6 to 1·2% of the fresh yeast. C. R. H.

Feeding of Plants with Aldehydes. V. Influence of Formaldehyde on the Function of Plant Enzymes. T. SABALITSCHKA (*Biochem. Z.*, 1924, **148**, 370—382).—Germination of seeds is inhibited more or less completely by 0·13% formaldehyde solution, whilst the growth of young twigs is somewhat affected by 4% solutions, and the fermentation of dextrose by living yeast is stopped by 0·3% formaldehyde and slowed by concentrations between 0·3 and 0·005%. In the cell sap of plants grown in atmospheres containing formaldehyde less than 0·055% of the aldehyde was found. In general, no evidence was forthcoming in support of the view that in such concentrations the aldehyde acts as a stimulant of plant metabolism. J. P.

Composition and Digestibility of Lupins and Lupin Offals, before and after the Removal of the Bitter Principle; and the Loss of Crude and Digestible Foodstuff resulting from Different Processes of Removal of the Bitter Substances. F. HONCAMP, E. MÜLLER, F. POMMER, and R. SOIKA (*Landw. Versuchs-Stat.*, 1924, **102**, 261—307).—Lupins, after removal of the bitter contents, have a high food value and the milling offals (excepting the "bran") are characterised by a high content of digestible protein. Losses in food value occasioned by the elimination of the bitter flavour, fall mostly on the nitrogen-free extractives, mineral matter, and to a less extent on easily soluble amides. The proteins are but little affected. A. G. P.

Lime Requirement of Soils, and a New Method of Mechanical Analysis. A. N. SOKOLOWSKI (*Arb. Wiss. Inst. Düngemittel*, 1923, **13**, 1—22; from *Chem. Zentr.*, 1924, i, 1584).—Adsorbed calcium is removed from soils by leaching with alkali salts. The soil thereby becomes deflocculated and water extracts from it an "active sediment" which is considered to be its most important constituent. Directions are given for the determination of this material in soils. From the content of a soil in adsorbed calcium

and its saturation capacity for calcium and ammonium respectively, a formula for the lime requirement is developed. G. W. R.

Effect of Manganese on Vegetation. G. D'IPPOLITO (*Staz. Sperim. agrar. ital.*, 1923, **56**, 386—400; from *Chem. Zentr.*, 1924, i, 952).—Marked increases in yield were obtained in pot and field experiments when manganese compounds were used as fertilisers. Manganese dioxide was more effective than manganic sulphate. G. W. R.

Determination of the Availability of Fertilisers. C. LUMIA (*Atti I. Congr. naz. Chim. pur. appl.*, 1923, 370—371; from *Chem. Zentr.*, 1924, i, 2003).—A method is proposed for determining the availability of fertilisers by comparing their effect with that of water-soluble fertilisers on the activity of brewer's yeast. G. W. R.

Dependence of Denitrification on the Reaction of the Medium. T. M. SSACHAROWA (*Arb. Wiss. Inst. Düngemittel.*, 1923, **15**, 1—22; from *Chem. Zentr.*, 1924, i, 2000).—In culture media the optimum reaction for denitrification lies between p_H 7·0 and p_H 8·2. This process does not occur below p_H 5·5 or above p_H 9·8. The optimum for the decomposition of nitrites lies between p_H 5·5 and p_H 7·0. G. W. R.

Chemical and Biological Studies with [Calcium] Cyanamide and some of its Transformation Products. K. D. JACOB, F. E. ALLISON, and J. M. BRAHAM (*J. Agric. Res.*, 1924, **28**, 37—69).—Under laboratory conditions, ammonification of calcium cyanamide in soil is rapid, but nitrification follows only slowly, probably owing to the formation of small quantities of dicyanodiamide which, when added to soil, inhibits the process of nitrification. Guanyl carbamide and guanidine salts also tend to inhibit nitrification. [Cf. *B.*, 1924, 842.] C. T. G.

Critical Note on Method of Correcting Protein Digestion Coefficients. H. E. WOODMAN (*J. Agric. Sci.*, 1924, **14**, 428—434).—The method of Pfeiffer for correcting "apparent" protein digestion coefficients for the undigested protein in the fæces is adversely criticised. Figures are recorded illustrating anomalous results which may be obtained by the adoption of this correction. A. G. P.